Application of Enhanced Desorption-Sorption as a New Process for Remediation of the Sediments

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Abstract

Application of Enhanced Desorption-Sorption as a New Process for Remediation of the Sediments

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Concordia University, 2019

Contamination of the sediments by organics and inorganics is a rising concern. However, remediation of contaminated sediments is complex and challenging.

As yet, the application of the enhanced desorption combined with the sorption for remediation of the contaminated solid media has not been investigated. In environmental research, few studies have focused on closed-loop remediation methods. This study was to evaluate a desorption-sorption process and the influential parameters for remediation of hydrocarbon-contaminated sediments. Also, it aimed to investigate the adsorption capacity of the sorbent (silica aerogel), adsorption isotherms and adsorption kinetics, as well as the fate of heavy metals, phosphorus and nitrogen, and regeneration of aerogels by solvents and heat in the desorption-sorption process.

A laboratory-scale system was designed and built for fast remediation of sediments. A strong turbulence vessel was used to increase the desorption of contaminants from sediments. A packed column containing hydrophobic silica aerogel granules was used to remove the contaminants from the effluent slurry.

The results showed 29.5% total petroleum hydrocarbon (TPH) removal from sediment after 45 minutes of vigorous agitation at 15900 rpm. The processed sediment and effluent water met Canadian governmental and provincial quality criteria. Higher agitation speeds (22100 rpm) increased the leaching of hydrocarbons from sediments by 31%.

In a warm environment (35^{o}C), the desorption of TPH from sediments was 28.9% higher than at ambient temperature (22^{o}C), but in a cold environment (10^{o}C), it was 16.3% lower than at ambient temperature. The sorption capacity of aerogels was increased from 9.6 mg/g at 22 ^{o}C to 10.5 mg/g at 10^{o}C but decreased to 6.7 mg/g at 35^{o}C. pH (5, 7 and 9), salinity (3.5%), solid load (5, 10 and 15 g/l) and retention time (11.5 and 26 seconds) did not show a significant effect on the efficiency

of the process. Adsorption data suggested a pseudo-second-order kinetics and a Freundlich adsorption model were the most appropriate.

The sediment quality including the content of investigated heavy metals (Cr, As, Cd, Pb, Cu, Zn, Ni, Mn, Co, Mo), nitrogen, and phosphorus did not change significantly after the desorption-sorption process. The concentration of heavy metals in the effluent water was significantly lower than the drinking and freshwater standards. Aerogels showed a low affinity towards the heavy metals but decreased the concentration of total phosphorus and total Kjeldahl nitrogen in water by 65% and more than 95%, respectively. Regeneration of the aerogels by organic solvents was not feasible. Repetitive regeneration by heat reduced the sorption capacity of aerogels. This research introduces a new environmentally-friendly methodology for remediation of sediments and other solid environmental media.

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Table of Contents

List of Figures

List of Tables

List of Abbreviations

AOPs	Advanced Oxidation Processes
ASTM	American Society for Testing and Materials
BTEX	Benzene, Toluene, Ethylbenzene and Xylene
COD	Chemical Oxygen Demand
DO	Dissolved Oxygen
EC	Electrical Conductivity
FEL	Frequent Effect Level
FID	Flame Ionization Detector
FTIR	Fourier Transform Infrared Spectroscopy
GC	Gas Chromatographic
HRT	Hydraulic Retention Time
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
LOI	Loss on Ignition
OEL	Occasional Effect Level
OMA	Oil-Suspended Particulate Matter Aggregates
PAH	Poly Aromatic Hydrocarbons
PCBs	Polychlorinated Biphenyls
PEL	Probable Effect Level
POPs	Persistent Organic Pollutants
PVC	Poly Vinyl Chloride
REL	Rare Effect Level
SEM	Scanning Electron Microscopy
TEL	Threshold Effect Level
TEM	Transmission Electron Micrograph Imaging
TGA	Thermogravimetric Analysis
TKN	Total Kjeldahl Nitrogen
TOC	Total Organic Carbon
TPH	Total Petroleum Hydrocarbon
UCM	Unresolved Complex Mixture
USCS	Unified Soil Classification System
USEPA	United States Environmental Protection Agency
VOCs	Volatile Organic Compounds

Chapter 1 - Introduction

1.1. Problem Statement: Sediment Contamination & Remediation

Contamination of the sediments by organics and inorganics is a rising concern. Risk assessment and remediation of contaminated sediments are among the most complex and challenging practices of environmental operation. Contaminants diffuse into the porous matrices and form strong bonds with sediments. Due to the strong attractive forces between the contaminants and solid matrix, the process of extraction, separation, immobilization or destruction of the contamination is sophisticated (Fingas, 2011; Mulligan et al., 2009; USEPA, 2005).

Sediments are a complex of inorganic, organic and biological matter. The composition and physical properties of a medium dramatically affect the type and difficulty of the remediation technique. Due to the occurrence of complicated physical, chemical and biological interactions, over time, the remediation of contaminants in sediments becomes difficult (Huesemann et al., 2006; Manahan, 2010). In fact, sediments are one of the most difficult environmental media for remedial actions. In the USA, at some sites, the volume of sediments that needs to be managed exceeds more than one million cubic meters (Fingas, 2011).

According to Fingas (2011), so far, no proven technique exists as containment for suspended oil in the water column or deposited on the bottom of the sea. The recovery methods for submerged oil spills are expensive, complicated and not very efficient. Mechanical remediation methods eliminate or minimize the necessity of addition of washing agents such as detergents and surfactants. Booms are usually the first means applied for containment of an oil spill. Booms can fail to perform due to the existence of wind, waves and water currents. Slurry reactors,

mechanochemical treatment, attrition scrubbers, cavitational remediation, ultrasound, jet scrubbers, and fluidized bed reactors are considered as mechanical remediation techniques. For the environmental operations, conventional mechanical methods are either energy-consuming (e.g. jet scrubbers), time-consuming (e.g. attrition scrubbers), cost-ineffective (e.g. ultrasound), sophisticated to control (cavitational remediation), difficult to scale-up (e.g. mechano-chemical treatment) or of low efficiency (e.g. attrition scrubbers). In addition, in many cases, the produced effluent contains high concentrations of contaminants with a need for further treatment before returning to the environment. Mechanical remediation methods are discussed in more detail in section 2.5.

The current remediation techniques bear their own pros and cons, which are briefly discussed in the following section. Some methods have only been studied and some are fully commercialized.

As yet, the application of the enhanced desorption combined with the sorption for remediation of the contaminated solid media has not been investigated. In environmental research, studies have not focused on closed-loop remediation methods. In the present research, hydrocarbon-contaminated sediments were studied for their behavior towards the enhanced desorption-sorption technique in the remediation of hydrocarbon contaminants.

1.2. Sorption and Enhanced Desorption in Environmental Remediation

Natural and synthetic sorbents such as zeolites, silicates, alumina, charcoal, activated carbon, and polymers have been broadly used for spill containment or cleanup (Noble & Terry, 2004). Sorbents are deployed to remove the pollution from the surface of an impermeable solid or bulk of a liquid or a gas phase. *In-situ* amendment of soil and sediments by mixing or capping with a sorbent has been researched and applied in the environment. The *in-situ* "sequestration" of the contaminant from soil or sediment by sorbent amendment is slow and it takes months and even years to complete (Ghosh et al., 2011; Qian et al., 2003). Amendment of sediments, e.g. by activated carbon, may cause an alteration in the benthic communities (both epibenthic and infaunal species) at the bottom of the water body (Qian et al., 2003).

Recently, different types of aerogels, particularly silica aerogels, as efficient adsorbents have received attention by environmental researchers. Aerogels, due to their physical and chemical properties such as high adsorption capacity, exceptionally lightweight, high porosity, strong chemical affinity, and harmlessness can be considered as reliable substitutions for conventional sorbents. Modified silica aerogels are nontoxic and bear a strong surface hydrophobicity (Norris & Shrinhasan, 2005). By lowering the costs of production, aerogels can be considered as ideal sorbents for removal of organic contaminations from the environment (Soleimani & Abbasi, 2008). It is forecasted that by the year 2020, the market size of aerogel production will increase to reach $230 million (USD) (Koebel & Zhao, 2013). In the present research, hydrophobic modified silica aerogel is used as an adsorbent to remove the hydrocarbon contamination from the sediments and water.

Exposing a contaminated solid media to the heat or a solvent with a higher affinity increases the rate of desorption to higher levels than sorption. This procedure can enhance decontamination of the solid media. Application of washing agents, detergents, solvents, heat and steam for releasing the hydrocarbon pollutants from the solid media have been studied extensively. These stimulators have been applied commercially for decades (ICS-UNIDO, 2007).

Applying mechanical forces to enhance washing the contaminants from the solid media is a well-known technique (Khan et al., 2004; Schwab et al., 1999). Vigorous shaking in combination with a solvent is a common method for extraction of hydrocarbon contaminants from solid media in laboratory measurements (Weisman, 1998).

1.3. Motivation of the Present Research

Sorption techniques have been commercially applied to strip the contaminant from the aqueous and gaseous phases. Unlike the wide variety of contamination adsorption techniques for fluids, sorbent amendment is the only applied adsorption method for remediation of solid media so far. There are only a few studies on silica aerogels for contaminant removal from water and air (Korhonen et al., 2011; Parale et al., 2011; Reynolds et al., 2001a & 2001b; Standeker et al., 2007; Standeker et al., 2009; Venkateswara Rao et al., 2007).

Aerogels have shown a high potential for adsorption of organic and inorganic pollutants. Silica aerogels are non-toxic and chemically inert, and therefore potentially could be applied in environmental remediation. The aerogel's surface can be modified towards a desired affinity to an individual or a group of contaminants. For oil spill containment, modification of the surface creates a very strong hydrophobic characteristic to adsorb the contaminants and repel the water. Aerogels are very light with a density of around one-tenth of water. The lightness allows separation quickly from the water and solid media by floating on the surface. In the present research, a modified silica aerogel having a highly-hydrophobic surface has been selected for adsorption of hydrocarbon contamination.

There is a gap in the studies on the application of a combined turbulence-sorption mechanism in a closed-loop system for remediation of solid media. Applying a closed physical-mechanical system for the elimination of contaminants from the solid media seems attractive. Utilizing a regular high-speed mixer, instead of an ultrasonic horn or a water-jet ejector, eliminates the need for a sophisticated control mechanism, reduces scale-up difficulties and avoids costly remediation facilities. Design of an ordinary mixing system, where there are enough knowledge and experience, is more convenient than an ultrasound or a jet cavitation generator. Furthermore, exploiting aerogels can restrain the release of pollutants into the environment. The system can operate *in-situ* or on-site. Accompanied by physical forces, aeration of the solid media generates a highly aerobic condition and enhances the decomposition of pollutants.

1.4. Objectives

The main aim of the present study was to investigate the behavior and efficiency of an enhanced desorption-sorption process as a new physical-mechanical remediation method for remediation of hydrocarbon contaminants in sediments. The other objectives were to determine:

- the effect of influential parameters including temperature, pH, salinity, solid concentration, retention time and agitation power;
- the adsorption capacity of aerogel at different water temperatures and pH
- the adsorption kinetics and isotherms;
- the mechanisms involved in the process;

- the physical and chemical change in sediment and aerogel granules;
- the change in sediment and water quality and the fate of heavy metals, phosphorous and nitrogen;
- the feasibility and efficiency of regeneration of aerogels;
- the comparison between the adsorption capacity of applied aerogel particles and conventional adsorbents;
- the comparison of the sorption-desorption method among the current and future remediation methods.

In order to examine the research hypothesis, a desorption-sorption process setup including a forced desorption chamber, an adsorption column, and a control panel was designed and built, and experiments were conducted with. The turbulence chamber was used as a desorption stimulator to detach the contaminants from the sediments. Hydrophobic surface-modified silica aerogel was used as an adsorbent to sorb the contamination. The setup design allowed measuring the effect of different factors on the efficiency of remediation.

The analysis of the collected data provides a deeper understanding about the interaction of solid-liquid and solid-solid media in turbulent regimes. As well, it introduces a new method for remediation of environmental solid media. Furthermore, it presents a clearer image for prediction of the effect of turbulence on desorption and sorption of contaminants e.g. in a flood event or storm run-off.

The enhanced desorption-sorption method was examined on the sediments contaminated with petroleum hydrocarbons. Sediments were characterized before and after the process. In the pre-specified time intervals, a slurry sample was taken and the content of hydrocarbon in the aqueous and solid phase was measured. Gas chromatography combined with a flame ionization detector (FID) was applied to measure the variation of hydrocarbon content in the sediment samples and water during the experiments. The change in pH, concentration of dissolved oxygen and electrical conductivity of sediment-in-water slurries was measured during the process. The effect of temperature, pH, salinity, solid load, retention time and agitation speed on the behavior of the process was studied. The adsorption capacities of aerogel and activated granular carbon from the hydrocarbon pure phase and oil-water emulsion were measured and adsorption isotherms and

adsorption kinetics were calculated. The effect of temperature and pH on the adsorption of aerogel was investigated. Power consumption at different agitation speeds was calculated. Scanning electron microscopy (SEM) was applied to observe the change on the surface of sediments and aerogels particles. Particle size analysis before and after the process was performed. Fluorescence Microscopy was performed to locate petroleum hydrocarbons in sediments. The regeneration of aerogels by solvents and heat was investigated by thermogravimetric analysis (TGA) and Fourier transform infrared spectroscopy (FTIR) methods. To investigate the change in the quality of sediments, the fate of heavy metals, phosphorous and nitrogen in sediments under the influence of desorption-sorption process were studied. The adsorption capacity of aerogels was compared with conventional adsorbents. Lastly, the desirability of sorption-desorption methodology was reviewed. The experiments were at least in duplicate to ensure the quality of the generated data.

1.5. Basic Assumptions and Limitations

Hypothetically, solid environmental media is not impenetrable. The surface of our planet is covered with a material, called “Regolith”, consisting of soil and sediment. Regolith is defined as a “loose” and incoherent material which covers the bedrock (Mathur, 2008; McConell & Abel, 2013; Pipkin et al., 2013). According to Mulligan et al. (2009), sediment is a “loose” macro-porous structure of aggregated flocs. The present study assumes that the mechanical forces can enhance the pace of desorption from the “loose” matrix of environmental solid media. If the solid media have open networks, then the strong impacts from macro- and micro-vortices of fluid would be able to enhance desorption of contaminants. Many contaminant-solid bonds may be very strong, so they cannot be weakened by a high fluid’s shear stress or physical impact.

Practically, a significant part of organic contaminants can be detached from solid media by washing accompanied by mechanical means e.g. vigorous turbulence or ultrasonic waves. In oil remediation, the fundamental assumption of solid washing is that though hydrocarbons are not very soluble in water, “they are not completely insoluble” (Cole, 1994). Currently, most soil and sediment washing processes use water. Raising the temperature or the addition of detergents, organic solvents, chelating compounds, surfactants, biosurfactants, acids, and bases facilitates dissolution and desorption of contaminants (ICS-UNIDO, 2007, Mulligan et al., 2001a & 2001c

& 2009). It is assumed that applying a mechanical impact can substitute the consumption of washing aids.

Also, it is assumed that a part of the hydrocarbon contaminants is transferred during solid-solid surface contact. On the other words, the contaminants desorb by the solid-solid collisions (Di Toro, 1985) and sorb through solid-adsorbent surface contacts. Furthermore, presumably contaminant hydrocarbons are immediately taken up due to the high affinity of the aerogel to enhance the quality and safety of the exiting slurry. Seemingly, the limitations appear in several occasions: where there is a very strong binding between the contaminant and the solid media; the porosity of the solid media is high, or the contamination has occurred a long time ago. Hence, the desorption-sorption technique does not lead to a significant efficiency. In a real-scale environmental operation, the desorption-sorption method may be applied for containment or remediation of the fresh low- to medium level of contamination in soil and sediments.

1.6. Thesis Overview

This thesis includes five chapters. Chapter 1 contains problem statement, motivation, objective, basic assumptions and limitations of this research. Chapter 2 discusses the hydrocarbon contamination in sediments. Also, it covers the theory and background of desorption and adsorption phenomena, their mathematical models, occurrence in the nature and application in environmental cleanup operations. Chapter 3 explains the material and methods including the design characteristics of the desorption-sorption process setup, measurements, and experiments. Results are represented and discussed in Chapter 4. Finally, Chapter 5 includes conclusions and recommendations for future studies.

Chapter 2 - Theory and Background

2.1. Oil Contamination and Its Hazards

In 2013, more than 11.5 million tons of crude oil and its products were consumed worldwide on a daily basis. In the same year, in Canada the daily consumption of oil and oil-derivatives was about 309,000 tons; whereas in the United States it was about 8.5 times more and exceeded 2,600,000 tons (Global Firepower). In 2011, the United States imported about 3 million tons of crude oil and derived products every day. Canada exported 600,000 tons and imported 100,000 tons of crude oil daily. About 350,000 oil wells are reported in Alberta and Saskatchewan producing the main portion of the Canadian oil. Twenty-two oil refineries operate in Canada (Fingas, 2011).

Spills caused by human error, equipment failure, accidents, and climate disasters regularly occur around the world. Spills happen during the well drilling, extraction, transport, storage, refining, downstream transforming, and usage. On average, for an oil-based product, there are about 10 to 15 transfers between the oil well and the final consumer. In each transfer, there is a risk for accidents, leakage or sabotage. In Canada and the United States, the minimum size of the spill which is obligatory to report is between 400 to 8000 liters varying from one to another region (Fingas, 2001).

According to Fingas (2001), the average cost of oil spill cleanup varied from $20 to $200 per liter of oil around the world. In the same year, the cost of oil spill cleanup was about $20 per liter of spilled oil in Canada. In the US, the cost was about $100 per liter. Cleaning of oil spills in the sea bottom is more difficult and expensive than on the land or in the water.

Petroleum hydrocarbons, their derivatives, and consumer products are among the most hazardous materials. Hydrophobic organic pollutants are recognized by high toxicity, slow rate of degradation and wide spreading in the environment (Reible & Lanczos, 2006). To draw a portrait for the extent of hydrocarbon pollution it is worthy to mention that one gallon of gasoline (containing 3% benzene) can contaminate millions of gallons of groundwater (Place et al., 2001). Volatile organic compounds (VOCs) are also among the soil contaminants. Benzene, toluene, xylene, and trichloromethane are some examples of VOCs (Manahan, 2010). Lighter fuels are more toxic but are less persistent; while heavier fuels are less toxic and remain in the natural systems for a long period of time. Aromatic rings are very toxic and very persistent (Brown et al., 2017; Fingas, 2011).

In the water bodies as well as soil and sediments, a portion of oil dissolves in the water and enters the body of living organisms very fast. The portion which is not soluble in the water can be absorbed within the fat tissues of living organisms (e.g., through the cell membrane or skin and enters the metabolic cycles). Generally, the solubility of oil in the water is low, but still, it is very important to be considered, since it may affect a part of the living environment (Fingas, 2011). Furthermore, high concentrations of oil must be removed manually or mechanically, otherwise, a highly viscous mousse can form during the time and hinder or stop natural cleaning processes (Bragg and Owens, 1995). In Canada, about 60% of contaminated sites involve contamination with petroleum hydrocarbons. Currently, these contaminated sites are over- and under-managed (CCME, 2008).

2.2. Hydrocarbon Contamination in Sediments

In the natural basins, sediments originate from erosion and weathering of the minerals, soil, and organic materials. Erosion can occur in the upstream of the water body or on the riverside. Sediments are a shelter for living aquatic species and the perfect environment for microbial processes. At the same time, sediments are a source and an ultimate sink for chemical and biological contaminants (Mulligan et al., 2009; Reible & Lanczos, 2006). According to the United States Environmental Protection Agency (USEPA), a contaminated sediment is defined as “sediment containing chemical substances at concentrations that pose a known or suspected threat

to environmental or human health" (USEPA, 1996). Sediments can release their content of contamination into the water body (van Noort et al., 2003).

About 1.2 million tons of oil enter the marine environment worldwide annually. Spills happen in water bodies or on land during extraction, transportation, storage, refinery, and processing operations (Fingas, 2011). In Canada, about 12 spills of more than 4000 liters happen every day in navigable waters. In the United States, about 25 spills of more than 4000 liters into the navigable waters happen per day. Oil spills from tankers are about less than 5% of all oil pollution entering the seas. The major source of oil pollution in the oceans is the run-off of fuel and oil from sources on land (Fingas 2001). Sediments act as a sink for pollutants. A major part of pollution in the water bodies sorbs onto the sediments lying at the bottom. The concentrations of pollutants in the sediments are higher than the contacting water by orders of magnitude. According to the USEPA, more than 750 million cubic meters of superficial sediments are seriously contaminated (Reible & Lanczos, 2006).

2.3. Sediment Remediation Methods

Numerous conventional methods are suggested for remediation of the sediments, though not all are commercially applied. The site characteristics, costs, type and quantity of contaminants and chemical composition of the sediments e.g. salts, sulfur and phosphorus compounds, amino sugars, nucleotides, and polysaccharides influence the selection of remediation process (Manahan, 1999; Mulligan et al. 2009 & 2001b).

Generally, *ex-situ* methods require high transportation costs as well as the risk of exposure and contamination of the environment. *In-situ* remediation methods are relatively less costly, due to a minimal disturbance in the natural environment and less risk of exposure of polluted media. However, the level of control is not as extensive as *ex-situ* processes; the extent of remediation is lower than *ex-situ* methods; and the knowledge of remediation still needs to be developed. Each individual method carries its own cons and pros. For instance, steam and high-temperature methods consume a large amount of energy. Transporting soil and dredged sediments need expensive mechanical operations. In general, traditional methods are time and/or energy consuming (ICS-UNIDO, 2007; Khan et al., 2004; Li, 2008; USEPA, 2005).

Unlike aqueous media, the variety of methods and influential parameters to be taken into the account for remediation of sediments is very large. The number of factors affecting the remediation process could be as large as all existing components, plus physical and environmental parameters. For instance, the composition of minerals, the content of organic matter, sorption affinity, porosity, hydraulic conductivity, particle size distribution, the mobility of contaminants and solids (particulate and colloid mobility) affect the type, duration, and extent of the remedial process (Mulligan et al., 2009; Weiner, 2000). In both contamination remediation and spill containment, one of the most important and primary actions is the removal of the source of contamination including both the free and attached phases. The presence of contaminants, particularly hydrocarbons, can interfere with all remediation attempts. If a method can remove the contamination source, it will be considered as an important advantage (Fingas, 2001).

Research has focused on the capability of innovative environmentally-benign methods. Bioremediation and phytoremediation have been applied to utilize the enormous capacity of living organisms for extraction or destruction of pollutants (Repas et al., 2012; Singh & Tripathi, 2007; Singh & Ward, 2004). Advanced oxidation processes (AOPs) include new methods based on hydrogen peroxide oxidation reactions. The combination of different means such as H_2O_2+UV, ultrasound+Fenton, photo-Fenton, ozone-based methods (O_3, O_3+UV, and O_3+catalyst), photolysis and photocatalysis fall under this category. Those methods have been studied in the treatment of aqueous media and rarely for soil. AOP methods mostly are not cost-effective in the real environment (Andreozzi et al., 1999; Esplugas et al., 2002; Pera-Titus et al., 2004; Saritha et al., 2007). “E-beam Technology” using high energy electron beams has been applied to destroy a wide range of organic pollutants by the efficiency of up to 99.99%, but mainly in the aqueous phase (Hamby, 1996; Tang, 2003). A series of experiments has been conducted to investigate the ability of microwave heating to strip volatile organic compounds (VOCs) form various media including water, wastewater, waste sludge, ore grinding tailings, soil, and sediment. The method has shown a high efficiency in the bench-scale, but it bears the shortcomings of the high rate of energy consumption, the elevated risk of exposure and higher costs of application in the environment (Jones et al., 2002). Gamma-ray irradiation, if the protective measures are placed properly, is considered as clean methods, but so far, all the experiments have been conducted on the aqueous media (Bank et al., 2008; Chitose et al., 2003; Gehringer & Matschiner, 1998; Lee & Lee, 2005; Mucka et al., 2000; Trojanowicz et al., 2012). Different types of non-thermal plasma,

including glow discharge, corona discharge, gliding arc discharge, dielectric barrier discharge, and spark discharge, have been studied for remediation of hydrocarbon-contaminated soils and water; though, as yet all experiments have been conducted at the bench- and pilot-scales. The high consumption of energy and the design difficulties in the reactor scale-up are two main bottlenecks in the commercialization of non-thermal plasma. Generally, due to the high capital and operating costs, most advanced techniques are not commercially applicable, as yet (Aggelopoulos et al., 2013; Jiang et al., 2014; Wang et al., 2010; Wang et al., 2014).

2.4. Sorption of Contaminants

In the following sections, the importance of the sorption in the environmental operations is discussed.

2.4.1. Sorption in the Natural Environment

The term "sorption" refers the uptake of an organic or inorganic contaminant from the surrounding environment into the matrix of the solid media. Sorption of radioactive elements into the plants, sorption of the sulfur oxides into the mist, sorption of hydrocarbons into the soil matrix and sorption of heavy metals into the river sediments are some instances of natural sorption in the environment.

In natural environments, many factors originating from the sorbent, solute or surrounding environment affect the rate and extent of the sorption of organic and inorganic contaminants. The concentration of solutes in all present media, relative affinity for each phase, hydrophilic or hydrophobic characteristics and electrical charges on the surface (polarity), number of surface-active sites, intermolecular forces, the presence of other ionized species and environmental conditions such as temperature and pH are among those factors. For soil and sediments, the content of organic matter in the pore water and the matrix has a significant effect on the mechanism and extent of sorption (Delle Site, 2001; Lick, 2009; Mulligan et al., 2009; ten Hulscher & Cornelissen, 1996; Weiner, 2000). The sorption phenomenon is applied in the cleaning processes in environmental protection and remediation (Chiou, 2002; Inglezakis & Poulopoulos, 2006; Mota & Lyubchik, 2008; Mulligan et al., 2009; Zhang et al., 2009).

If the concentration of solute in the fluid remains constant or declines, due to the decrease in the concentration gradient between the fluid and solid, over time the rate of adsorption decreases and the rate of desorption increases. This phenomenon continues until an "equilibrium state" is reached. In the equilibrium state, the rates of adsorption and desorption are equal. In the same manner, in natural environments, the desorption process may accompany the sorption (Weiner, 2000).

2.4.2. Models of Adsorption

Adsorption may occur in sub-monolayer, monolayer and multilayer patterns (Chiou, 2002). In a molecular-size view, "absorption" is the phenomenon when the adsorbate moves between the molecules, atoms or ions of the adsorbent, while the "adsorption" occurs on the surface layers of adsorbent (Inglezakis & Poulopoulos, 2006).

Three different mechanisms govern bonding of the contaminants to a solid media (Bayley & Biggs, 2005a);

- Chemical bonds between reactive groups in the contaminant and the solid (i.e. chemical sequestration), e.g. reactions between the contaminant and the humic matter in the soil or sediment
- Weak inter-molecular forces between the contaminant and the solid such as van der Waals, hydrogen bonding and dipole-dipole bonding
- Partitioning (dissolving) of the contaminant into the solid phase, e.g. dissolution in the natural organic matter.

There is a relationship between the concentrations of the solute in different phases. Adsorption isotherms are equations between the amounts of adsorbate that adsorbed by adsorbent versus the concentration of that compound in the bulk of gas or liquid exposed to the adsorbent. The term "isotherm" refers to an important assumption of adsorption theory stating that the equilibria reach at a constant and similar temperature. To explain and predict the behavior of substances during adsorption phenomenon, numerous studies have been performed. Among the suggested mathematical simulations, isotherm models are classified as four major types (Figure 2.1). The

shape of the isotherm diagram provides some information about the interaction between the adsorbate and adsorbent (Somasundaran, 2004).

- **L-type**

L-type isotherm is known as a Langmuir isotherm and represents a relatively high affinity of adsorbate to adsorbent, usually chemisorption.

- **S-type**

The S-type isotherm represents a cooperative adsorption and occurs when adsorbate-adsorbate interactions are stronger than adsorbate-adsorbent interactions. In this condition, molecules of adsorbate make clusters at the surface of adsorbent.

- **C-type (Constant partitioning)**

The C-type isotherm represents a constant relative affinity of the adsorbate to adsorbent. This type of adsorption occurs at low extents of adsorption. When a high quantity of adsorbate adsorbs on the surface of adsorbent, a deviation from the linear behavior occurs. Many non-polar organic compounds adsorb in low concentrations on the solid phase and follow this pattern of adsorption (Somasundaran, 2004).

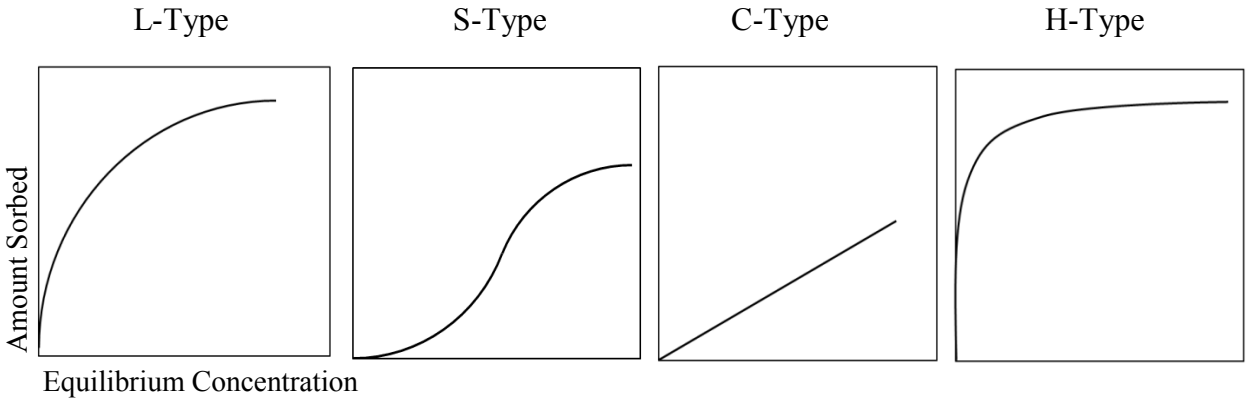


Figure 2.1. Four main types of adsorption isotherm (Somasundaran, 2004)

- **H-type**

H-type adsorption reveals very strong interactions between adsorbate and adsorbent i.e. chemisorption. The H-type adsorption may be considered as an extreme case of L-type. This type of isotherm does not represent adsorption of organic molecules because only few organic compounds make strong covalent or ionic bonds with solid. More complicated isotherm diagrams are hybrids of these four types of isotherms. Isotherm curves provide only suggestions for the mechanism of adsorption and are not considered as a proof for the mechanism (Somasundaran, 2004).

Adsorption Equations

Three models have received attention due to their simplicity and relative accuracy. These three models are described below (Chiou, 2002; Wang, 2011).

- **Langmuir Adsorption Isotherm**

According to Langmuir (1918), adsorption occurs on some active sites of the adsorbent. Drawing the Langmuir isotherm illustrates an L-type diagram. The equation can be written as:

$$Q = \frac{Q_m bP}{1 + bP} \qquad \text{Eq. 2.1}$$

In which:

Q = Amount of the component adsorbed by a unit mass of the solid

Q_m = Limiting adsorption capacity (monolayer)

P = Equilibrium partial pressure or concentration of adsorbate

b = k_a/k_d

k_a = Adsorption rate constant

k_d = Desorption rate constant

The constants Q_m and b in the Langmuir equation may be determined by rewriting Equation 2.1 as:

$$\frac{1}{Q} = \frac{1}{Q_m bP} + \frac{1}{Q_m} \qquad \text{Eq. 2.2}$$

- **Freundlich isotherm equation**

The Freundlich equation empirically relates variation in adsorption with the concentration of an adsorbate (solute or vapor) on a surface:

$$Q = \mathrm{k}C^n \qquad \text{Eq. 2.3}$$

where

Q = amount of adsorbate adsorbed per unit mass of the solid

C = vapor or solute concentration at equilibrium

k = Freundlich constant equal to the adsorption capacity (c=1)

n = an exponent related to the intrinsic heat of solute adsorption. It is mainly less than 1.

- **Brunauer-Emmett-Teller Adsorption Isotherm**

The Brunauer-Emmett-Teller model is an extension of Langmuir theory for multi-layer adsorption. The BET model is based on three assumptions: adsorbate molecules can be infinitely adsorbed on the surface of adsorbent by physical sorption, no interaction exists between layers and for each layer the Langmuir model is valid. The model can be expressed as:

$$Q = \frac{AC_e x_m}{(C_s - C_e)[1 + (A-1)\frac{C_e}{C_s}]} \qquad \text{Eq. 2.4}$$

in which

A = a constant which depends on the interaction forces between adsorbate and adsorbent

X_m = a constant dependent on the amount of adsorbate adsorbed in a complete monolayer

C_e = equilibrium concentration of solute

C_s = saturation concentration of adsorbate

Adsorption Kinetics

There are two well-known and frequently-applied adsorption kinetic equations: pseudo-first-order (Equation 2.5) and pseudo-second-order (Equation 2.6) (Gautam, & Chattopadhyaya, 2016).

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad \text{Eq. 2.5}$$

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \qquad \text{Eq. 2.6}$$

where

q_e = amounts of adsorbate adsorbed by adsorbent at equilibrium (mg/g)

q_t = amounts of adsorbate adsorbed by adsorbent at time t (mg/g)

k_1 = pseudo-first-order adsorption rate constant (min^{-1})

k_2 = pseudo-second-order adsorption rate constant (g/mg·min)

t = time (min)

For the purpose of data-fitting, Equation 2.6 can be integrated and rearranged as:

$$\frac{t}{q_t} = \frac{1}{(k_2 \times q_e^2)} + \left(\frac{1}{q_e}\right) \times t \qquad \text{Eq. 2.7}$$

2.4.3. Sorption Technology in Environmental Remediation

Sorption is one of the key remediation technologies in the present and future (Yang, 2003). Few examples of applications of adsorption in environmental engineering include the removal of organics from water, removal of radon, VOCs and hydrogen sulfide from gases, removal heavy metals from groundwater and removal of phosphorous, nitrogen, taste and odor from wastewater (Crini & Badot, 2010; Cooney, 1999; Inglezakis & Poulopoulos, 2006; Mota & Lyubchik, 2008; Zhang et al., 2009). Biosorption (i.e. the sorption of contaminants by microbial biomass) is used for various purposes for removal of the contaminants from wastewater to recover the precious metals (Aksu, 2005; Vijayaraghavan & Yun, 2008; Won et al., 2014). A large variety of adsorbents

are used in environmental containment and cleanup. Table 2.1 represents a short list of more common adsorbents. Activated carbon is the most commercially used adsorbent with worldwide sales of $380 million per year. The wide range of adsorbents falls in three categories based on their material entity: natural sorbents, chemically-modified natural sorbents and synthetic sorbents (Cojocaru et al., 2011; Sittig, 1974). Many original research studies and comprehensive reviews exist on the application of various sorbents in the environmental remediation (Ahmad et al., 2010; & 2011; Bhatnagar & Sillanpää, 2010 & 2011; Crini & Badot, 2010; Demirbas, 2009; Gupta et al., 2009; Kulprathipanja, 2010; Sharma et al., 2011).

2.4.4. Amendment of the Sediments by Sorbents

Sorbents have been used as amendment materials for remediation of sediments and soil. Sorbents can extract and hold the contaminants leaching from the soil or sediments. This process is known

Table 2.1. Common adsorbents and their characteristics (Noble & Terry, 2004)

Adsorbent	Characteristics	Nature
Activated carbon	Hydrophobic surface favors organics over air or water	Hydrophobic
Caron molecular sieves	Separates on the basis of different intra-particle diffusivities	Hydrophobic
Silica gel	High capacity	Hydrophilic
Activated alumina	High capacity	Hydrophilic
Zeolite molecular sieves	Hydrophilic surface, polar, regular chemicals	Hydrophilic
Silicalite	Hydrophobic surface, adsorption characteristics like those of activated carbon	Hydrophobic
Polymer adsorbents	Usually styrene	Hydrophobic

as sequestration. The word sequestration is defined as the trapping of a pollutant or transformation to a nontoxic or non-bioavailable form (Zimmerman et al., 2004).

Activated carbon is the most common applied sorbent. Zeolites, clays, organoclays, bentonite, bauxite, coke, coal, amberlite and biopolymers have been utilized, as well (Chai, 2004; Jacobs & Forstner, 1999; Knox et al., 2008; Li et al., 2009; Lin et al., 2011; Mahabadi et al., 2007; McDonough et al., 2007; Mulligan et al., 2009; Shi et al., 2009; USEPA, 2013). The remaining portion of the pollutant in the sediment and the potential for diffusive leaching in the future are among the drawbacks of the amendment method (Mulligan et al., 2009).

Mohan et al. (2000) reviewed mathematical models and design criteria for applying caps on the contaminated sediments. They reported that various mechanisms of transport phenomena in combination with affecting hydraulic and geotechnical parameters such as diffusion, advection, dispersion, particle settlement, solid filtration and stability of suspensions are important in a cap design. Paller & Knox (2010) studied potential hazards arising from the usage of organoclay, apetite, and biopolymers as active cap amendments for sediment remediation. They selected a few types of both fresh and saltwater organisms. The results showed that none of these materials leached toxic substances into the environment but in the cap containing biopolymers, organisms died due to entrapment and suffocation.

Uchimiya et al. (2011a & 2011b) studied the effect of soil properties on the sorption and desorption of copper species during amendment by biochar. They suggested cation ion-exchange with calcium and aluminum compounds in the soil as the main mechanism for copper sorption. Concurrent release of copper may be attributed to the acid dissolution of species. A study performed by Cho et al. (2009) focused on the use of activated carbon for *in-situ* stabilization of polychlorinated biphenyls (PCBs) in sediments. Between 2.0 to 3.2 wt% of a carbon amendment was incorporated into the sediment layer to a depth of 30 cm. The measurements showed a 50% PCB reduction in the sediments as well as in the pore water after 7 months of exposure. The same measurements after 18 months indicated 90% reduction of the PCB concentration. In a similar study, Millward et al. (2005) investigated the effect of activated carbon amendment applied for reduction of PCB bioaccumulation on the sediment benthic biota. The experiments showed that after 30 days of amendment exposure, the PCB bioaccumulation was reduced between 70 - 82 % in the different species of organisms.

2.4.5. Sorbents for Hydrocarbon Cleanup

Sorbents are an important means in the oil spill cleanup operations (Al-Majed et al., 2012; Dave & Ghaly, 2011; Fingas, 2011; Wu et al., 2014). Oil spill disasters such as rig explosions in Mexico Gulf in 2010, Kuwait 1991 and Exxon Valdez incident in 1989 revealed the importance of oil sorbents in spill containment and removal (Teas et al., 2001; Wu et al., 2014). In an oil spill, sorbents are used in four different occasions (Fingas, 2011):

- A primary option for oil recovery in the small spills;
- A backup method to the other containment methods;
- Removing the last traces of the oil spilled on the land or in the water; and
- A passive cleanup tool.

Sorbents are available in diverse forms and packaging: cubes, granules, blankets, rolls, pillows, pads, sweeps, booms, chunks and powders packed in socks, nets or bags. Synthetic sorbents have increasingly received attention in the last years (Fingas, 2011). Table 2.2 represents the necessary properties of a sorbent for application as oil spill containment in the environment.

Foam, straw, peat moss, wood product, polymers, talc, clay, dried volcanic rocks or cotton waste are used as adsorbents for oil removal. Table 2.3 represents the sorption capacity of suggested sorbents for the separation of oil from water (Fingas, 2011; Sittig, 1974). Polypropylene fiber mats with sorption capacity of 5 times their weight are commercially used for the oil spill cleanup. However, the oil retention capacity sharply declines to about 50% when the oil is removed from the mats (Korhonen, et al., 2011). Unmodified natural sorbents adsorb large amounts of water. Many wood-derived sorbents, untreated peat moss, and many inorganic sorbents tend to sink after they absorb large quantities of water. Sinking a sorbent with adsorbed oil causes serious harm to the benthic life at the bottom of the water body. Some countries have banned the use of sinkable sorbents (Fingas, 2011).

Materials such as polyethylene and polypropylene can float on the surface of the water (Fingas, 2011; Sittig, 1974). The boom in nanotechnology science and industry has brought the interest of environmental researchers to the nanostructured sorbents. Currently, nanosorbents are being investigated and gradually commercialized (Avila et al., 2014; Kharisov et al., 2014).

Table 2.2. Necessary properties of a sorbent for oil spill containment (Sun, 2010; Wahi, 2013; USEPA, 2007a; USEPA, 2014)

Property	Description
Oleophilic	The adsorbent should have a larger affinity to oil than water.
Hydrophobic	The material should reject or repel the water.
Adsorptive	Oil product should adhere to the surface.
Absorptive	Oil must be assimilated into the adsorbent.
High capacity	The ratio of oil adsorption should be 5:1 or preferably 10:1 by w/w scale.
Retentive	After collecting the adsorbent, leaching of oil should be low.
Fast acting	The adsorption process needs to take place quickly.
Cost-effective	The adsorbent should have a reasonable price for use.
Buoyant	The adsorbent should stay afloat in all conditions.
Non-toxic	Introduction of adsorbent that does not cause harm to the environment.
Easy collection	Adsorbent needs to be collectible with a regular effort.

Table 2.3. List of several suggested and commercial sorbents for separation of oil from water (g/g sorbent)

Sorbent Type	**Light Crude**	**Heavy Crude**
Synthetic Sorbents		
polyester pads	9	12
polyethylene pads	30	35
polyolefin pom-poms	3	3
polypropylene pads	8	10
polypropylene pom-poms	6	6
polyurethane pads	20	40
Natural Organic Sorbents		
bark or wood fiber	3	3
bird feathers	3	3

peat moss	3	4
treated peat moss	6	8
straw	3	3
vegetable fibre	4	4
Natural Inorganic Sorbents		
clay (kitty litter)	3	3
treated pearylite	8	8
treated vermiculite	3	4
Vermiculite	2	3

Application of sorbents provides the significant advantage of deletion of contaminant from the environment (Korhonen, et al., 2011). Spreading of sorbents is a relatively simple task. Personnel don't require extensive training. There are plenty of options for sorbent selection. Sorption may provide the ability of the recovery of the contaminant. On the other hand, sorbents require regeneration; the network structure deteriorates, and retention capacity gradually diminishes (Inglezakis & Poulopoulos, 2006). Even though sorbents are currently used in the oil spill cleanup operations, they are difficult to handle after oil adsorption (Prendergas & Gschwend, 2014).

Regardless of the commercialization of sorption methods for oil spill containment, the research is still ongoing. A review of the application of porous materials in the oil spill cleanup has been done by Adebajo et al. (2003). Choi & Cloud (1992) applied natural sorbents for oil spill cleanup studies. They found that milkweed is capable of sorbing about 40 grams of crude oil per 1 gram of fiber. Carmody et al. (2007a) studied the adsorption of hydrocarbons on the organoclays. They used three common soil pollutants including engine oil, hydraulic oil, and diesel to evaluate the behavior of organoclays. They found that the type of surfactant applied for the synthesis of the organoclay affects the capability of adsorption. They recommended the application of organoclays for oil spill containment pointing to their hydrophobicity, high affinity and retention capacities; but cost, the biodegradability, and recyclability of the organoclays are their drawbacks. Sayed & Zayed (2006) evaluated the efficiency of three different natural adsorbents from various typical industries in oil spill containment: sludge, garlic, and onion peel. The results showed that the highest adsorption capacity belonged to the chemically treated sludge equal to 2 grams per gram of adsorbent.

Carmody et al. (2007b) investigated the adsorption isotherms for several common adsorbents: sand, cotton, and organoclay. They attributed the adsorption capacity of these materials to the volume of pores and capillaries. Cotton represented a better option rather than sand and organoclay. In cotton, the presence of wax on the fibers enhances the oil uptake due to providing more hydrophobicity and low energy surfaces inside the capillaries. The efficiency of 5 different adsorbents, including 3 types of expanded perlite, cellulosic fiber from processed wood and polypropylene was investigated by Teas et al. (2001). Three different oils were used in dry and simulated seawater conditions in adsorption experiments. The highest adsorption capacity from sea water resulted from polypropylene and cellulosic fiber. In dry conditions, polypropylene had the largest oil uptake.

Payne et al. (2012) investigated the affecting parameters on the adsorption of a simulated crude oil by cellulosic fibers from different types of wood. The highest sorption capacity resulted from using bleached softwood kraft fiber, about six times the sorbent dry weight. This sorption capacity distinctly decreased when the fibers were exposed to the water. Kundu & Misha (2013) optimized removal of oil from an oily wastewater by a packed column of an oleophilic ion-exchange resin, Purolite OL-100. According to their results, the best parameters for the oil removal were the initial oil concentration of 30% (v/v), pH 6 and the emulsion flow velocity of 127×10^{-3} dm^3/min. Applying these conditions resulted in 83.4% of oil removal efficiency. Similarly, Maiti et al. (2011) applied a packed bed of a commercial resin, a co-polymer of styrene and divinylbenzene, for oil removal from an oil-in-water emulsion. In the optimized condition of 10 dm^3/h flow velocity and 500 mg/dm^3 influent emulsion, about 89% of the emulsified oil was removed.

2.4.6. Aerogels in Environmental Remediation

The term “aerogel” was introduced by Kistler (1932) to describe his invention, a gel in which the liquid was replaced by a gas while the solid network remained intact. Kristler’s gel was produced by supercritical drying of a silica-based gel. After him, the term “aerogel” represents every dry gel with a very high pore volume, typically about 90% (Aegerter et al., 2011). The Concise Encyclopedia of Composite Materials describes aerogels as “highly porous solid materials with very low densities and high specific surface areas” (Mortensen, 2006). Encyclopedia of Materials depicts their structure as a solid network of branched mesopores (i.e. fine similarly-sized pores).

This conformation results in very interesting physical properties. Because of their high degree of porosity, aerogels are extremely light, mostly transparent and bear very low thermal conductivity.

Aerogels can be fabricated in blocks, films, granulates or powders from organic or inorganic precursors (Buschow et al., 2001). To date, aerogels are considered one of the lightest synthetic materials on the earth. Silica aerogels are the most prominent type of aerogels and because of their high sorption capacity and non-toxic nature explored and experimented more than the other types. Silica aerogels also are known as “solid air”, “solid smoke” or “frozen smoke” (Figure 2.2) (Griffin, 2014; Tomczyk, 2014).

The network skeleton in silica aerogels is based on the silicon-oxygen bridges ($\equiv Si - O - Si \equiv$) as represented in Figure 2.3a (Gurav et al., 2010). Figure 2.3b demonstrates a scanning electron micrograph (SEM) of silica aerogel particles. The main properties of silica aerogels are listed in Table 2.4.

Following the discovery of silica aerogel, other types of aerogels have been invented after Kistler (Aegerter et al., 2011). Examples of other types of aerogels are carbon aerogels (Pierre & Pajonk, 2002, Tao et al., 2008), carbon nanotube aerogels (Zou et al., 2010), inorganic hollow nanotube aerogels (Korhonen et al., 2011), organic polymer aerogels (Pierre & Pajonk, 2002; Tao et al., 2008) alumina aerogels (Pierre & Pajonk, 2002), gold aerogels (Anderson et al. 1999), clay aerogels (Gawrya, 2009), chromium and tin dioxide aerogels (Kalebaila, 2007), cellulose nanofiber aerogels (Paakko et al., 2008) and silica aerogel-activated carbon composites (Mohamm-

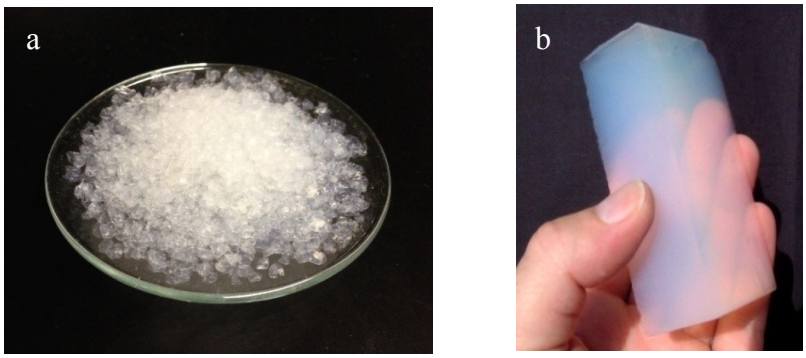


Figure 2.2. (a) Cabot aerogel granules applied in the present study; (b) Monolithic aerogel (Ecofine Nanotechnologies) (2016)

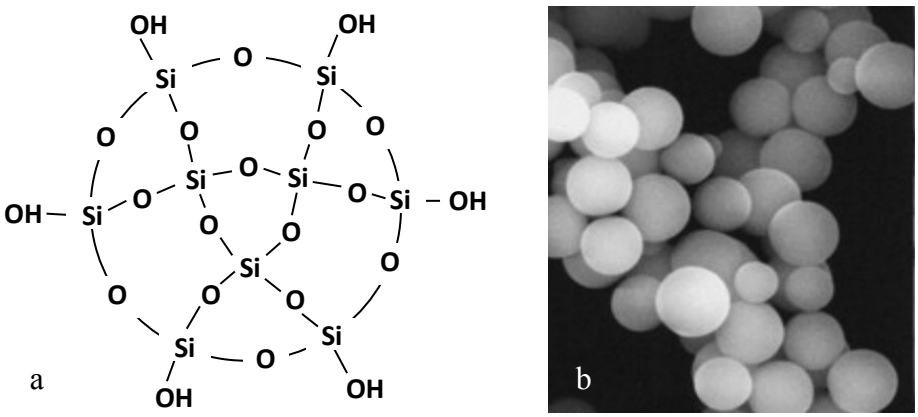


Figure 2.3. (a) Representation of the Si-O skeleton in silica aerogel (Gurav et al., 2010); (b) Representation of the porous structure of silica aerogel in a TEM image (Soleimani & Abbasi, 2008)

Table 2.4. Typical properties of silica aerogel (Norris & Shrinhasan, 2005)

Property	Value
Apparent density	0.03-0.35 g/cm^3
Internal surface area	600-1000 m^2/g
Content of solids	0.13-15%
Mean pore diameter	~ 20 nm
Refractive index	1.0-1.08
Coefficient of thermal expansion	2.0-4.0 x 10^{-6}
Dielectric constant	~1.1
Sound velocity	100 m/s

adi & Moghaddas, 2014). Recently, green chemistry methods for production of silica aerogels from natural products have been innovated: Aerogels made based on the rice hull (Tajarodi et al., 2012; Tang & Wang, 2005; Li & Wang, 2008), bamboo leaf (Kow et al., 2014), lignin (Grishechko, 2012), alginate (Alnaief et al., 2011), polysaccharides (Garcia-Gonzalez, 2011), and nanocellulose (Korhonen et al., 2011) are some instances.

Aerogels may be utilized in a wide range of applications (Carlson et al., 1995; Fricke & Tillotson, 1997; Herrmann et al., 1995; Hrubesh, 1998; Schmidt & Schwertfeger, 1998). They are applied for thermal insulation, space exploration (cosmic dust collection), optical applications (windows), acoustic insulation, catalysis, electronics (biosensors, biochips), encapsulation medium (drug delivery), solar cells and batteries (Aegerter et al., 2011; Akimov, 2003; Alnaief et al., 2011; Gao et al., 2009 & 2012; Gurav et al., 2010; Norris & Shrinhasan, 2005; Pierre & Pajonk, 2002; Smirnova et al., 2005; Supakij, 2005). However, despite the strengths, silica aerogels are very brittle, and the cost of fabrication is still higher than many other sorbents. The effort is ongoing to lower the production cost (Korhonen, et al., 2011; Soleimani & Abbasi, 2008).

Sol-Gel Process

Aerogels are made by substitution of the liquid part of a gel with a gas. The liquid content of the gel is extracted in a very slow pace to prevent the solid matrix to collapse. Traditionally, aerogels undergo a super-critical drying process. Xerogels are structures similar to aerogels but they are dried by regular evaporation; so, the shrinkage of the network occurs. Cryogels are a family of aerogels produced by a freeze-drying step (Pierre & Pajonk, 2002). The chemical equation for the formation of silica gel from tetraethylorthosilicate may be written as (Innocenzi & Kessler, 2008):

$$Si(OCH_2CH_3)_{4\,(liq.)} + 2H_2O_{\,(liq.)} = SiO_{2\,(solid)} + 4HOCH_2CH_{3\,(liq.)}$$

Aerogels are fabricated by a sol-gel process. Sol is a colloidal suspension of particles and the "gel" is a three-dimensional highly porous solid network. A sol-gel mixture is a gel that is produced from a sol. The sol-gel process is illustrated in Figure 2.4a (Norris, 2011; Norris & Shrinhasan, 2005). According to Alnaief (2011) for the production a silica aerogel a sol-gel process includes 4 steps as follows (Figure 2.4b):

- Dissolution. Addition of $Si(OCH_2CH_3)_4$, catalyst and ethanol and adjusting the reaction condition.
- Sol formation / hydrolysis. Addition of water
- Gel formation (condensation). Formation of three-dimensional network
- Drying. Supercritical (with CO_2) or atmospheric drying.

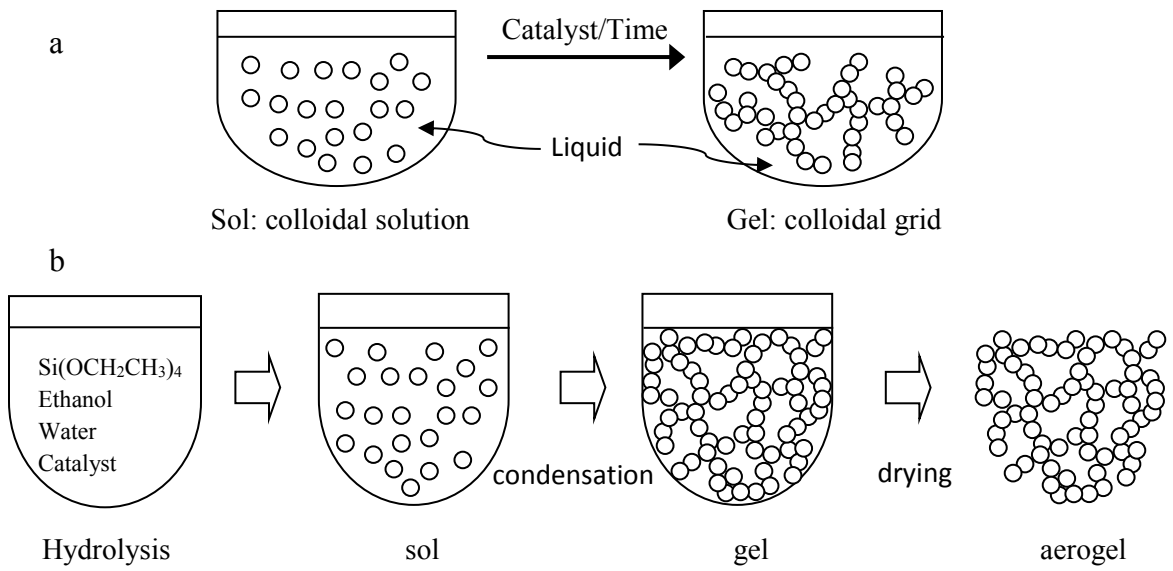


Figure 2.4. (a) Transformation of sol to gel (Pierre & Pajonk, 2002); (b) Four-step procedure for fabrication of silica aerogel (Alnaief, 2011)

Surface modification

After drying, the aerogels may be modified by some chemicals to introduce the hydrophobic characteristics to the surface. In silica aerogels (-OH) groups on the surface are substituted by trimethylsilyl-oxy [-O-Si(CH_3)$_3$] groups. The resulted modified silica aerogel is extremely hydrophobic and strongly repels water, bearing the capacity to be applied as a hydrocarbon adsorbent (Figure 2.5) (Soleimani & Abbasi, 2008).

Aerogels in Environmental Cleanup

Silica aerogels could be a potential alternative for activated carbons (Standeker et al., 2009). The possible applications of aerogels for environmental cleanup have been investigated by exposure to the various contaminants. Maleki (2016) has reviewed the research on the application of different types of aerogels in sorption of pollutants from the environment (Table 2.5). Due to high sorption capacity and low toxicity, the family of silica aerogels is investigated more than others. Parale et al. (2011) studied

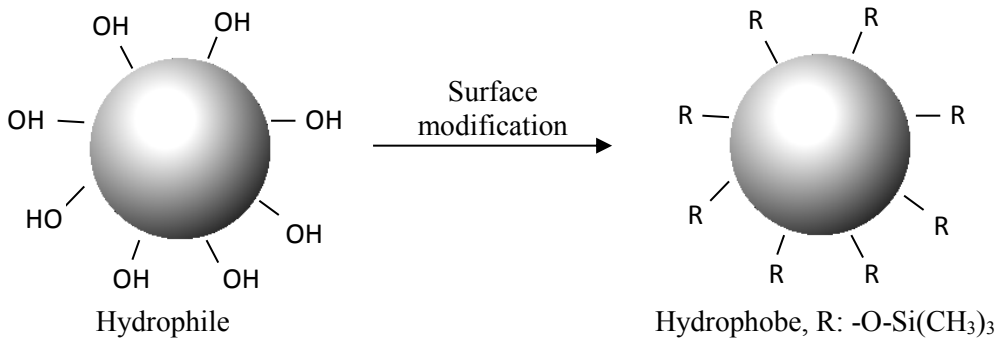


Figure 2.5. Replacement of hydroxyl groups with trimethylsilyl-oxy groups in silica aerogel during surface modification (Soleimani & Abbasi, 2008)

the adsorption and desorption of a wide variety of hydrocarbons on the silica aerogel granules. They used hexane, heptane, octane, cyclohexane, methanol, ethanol, propanol, isobutanol, benzene, toluene, xylene, acetone, petrol, diesel and engine oil. The results showed the capability of silica aerogels to rapidly adsorb about 10 to 15 times its weight.

Scanning electron microscopy (SEM) studies revealed a uniform network with about 97% porosity. The adsorption occurred by the capillary forces and was dependent upon the surface tension and density of hydrocarbons. Lower density and smaller surface tension resulted in the lower adsorption mass. Observations showed that adsorption of oil caused shrinkage in the aerogel network; while adsorption of solvent did not leave a significant effect. The hydrocarbon desorption time decreased by increasing the temperature. Also, after total desorption, silica aerogel resumed 80% of its preliminary structure.

Korhonen et al. (2011) studied the application of a hydrophobic nanocellulose aerogel as an oil adsorbent from the water. They coated nanocellulose aerogel with a nanoscopic layer of titanium oxide, an oleophilic substance, to produce an oil sorbent. The nanocellulose had a density of 20–30 mg/cm^3 and porosity of larger than 98%. The aerogel was able to adsorb 80-90% vol/vol or 20–40 wt/wt of the spilled oil. The organic contaminants could easily be washed out by an organic solvent such as ethanol. The aerogels did not show a change in the oil adsorption capacity after repeated immersion and desorption.

Table 2.5. Aerogels with their absorbed substances and sorption capacities (Maleki, 2016)

Sorbent aerogels	Absorbed substances	Sorption capacity
Cabot Thermal Wrap (TW) and Aspen Aerogels Spaceloft (SL).	Iraq and Sweet Bryan Mound oils	14.0 ± 0.1 and 12.2 ± 0.1 g/g (TW) 8.0 ± 0.1 and 6.5 ± 0.3 g/g (SL)
Carbon aerogel	C. I. Reactive Red 2 (dye)	1.14 mol/g
Carbon microbelt aerogel	Oils	56-188 times of its weight
Starch derived carbon aerogel	Crystal violet Methyl violet Methylene blue	1515 mg/g 1423 mg/g 1181 mg/g
Carbon aerogel	Toluene	1180 mg/g
Cellulose aerogel	Waste engine oil	11 to 22 times of aerogel's dry weight
Titania aerogel	Azo-dye Orange II	420 mg/g
-Montmorillonite clay-polymer composite aerogels-pure -Montmorillonite clay-polymer composite aerogels-hydrophobized with TMOS	Dodecane motor oil Dodecane motor oil Dodecane motor oil Dodecane motor oil	23.63 g/g 25.84 g/g 2.25 g/g 10.56 g/g
Magnetic graphene aerogels	Dyes and gasoline	16 to 22 times of its weight
Graphene aerogels	Oils and organic solvents	120 to 200 times of its mass
Graphene aerogel	Oils and organic solvents	11.200% of its weight
Clay-hybrid aerogels	-Organic dyes (methylene blue and malachite green) -Volatile organic pollutants (phenol and toluene) -Petrochemical derivatives (kerosene, engine oil, and diesel)	101.55, 98.42, 116.75 and 114.10 mg/g for methylene blue, malachite green, phenol, and toluene, respectively
Particulate hydrophobic silica aerogel (Cabot Nanogel@)	Liquid oils	15.1 g/g
Magnetic cellulose aerogel	Oils	28 times of its weight
Magnetic graphene aerogel	Motor oils	27 times of its weight
Hydrophobic silica-based aerogels and xerogels	Toxic organic solvents	192.31 mg/g
Graphene-carbon nanotube aerogels	Petroleum products, fats, and organic solvents	28 L of oil per gram of aerogel.

Poly(alkoxysilane) organogels	Oils and crude oils	295% for hexane, 389% for euro diesel, 652% for gasoline, 792% for benzene, 792% for toluene, 868% for tetrahydrofuran (THF) 1060% for dichloromethane (DCM)
-Hydrophobic silica xerogels -Hydrophilic silica aerogels	-Dieldrin -RhB	460 µg/g 34 mg/g
Hydrophobic granular silica aerogels	Phenol	142 mg/g

Quevedo et al. (2009) studied the removal of vegetable oil from water in an inverse fluidization bed. They used hydrophobic surface-treated silica aerogel granules in a fluidized mode created by a downward flow of water. The hydrodynamic characteristics of the inverse fluidized bed were studied by measuring the bed expansion and pressure drop in different superficial velocities. The oil removal efficiency of the aerogel was dependent on the on the size of the granules, the void fraction of bed and the fluid velocity. The pressure drop in the aerogel bed was very small so the energy consumption in the process was extremely low. The aerogel bed dramatically reduced the concentration of the oil in water from about 2000 mg/l to less than 10 mg/l.

Reynolds et al. (2001a, 2001b) in two different studies synthesized and investigated a hydrophobic CF3-functionalized silica aerogel for crude oil cleanup from salt water. The synthesized aerogel showed a sorption capacity of up to 237 times (wt/wt) in a dry condition and up to16 times (wt/wt) from an oil-water mixture.

Venkateswara Rao et al. (2007) studied the mechanisms of adsorption of organic liquids on the surface of an elastic silica aerogel. They synthesized an elastic monolithic silica aerogel using methyltrimethoxysilane as a precursor. Hydrocarbon adsorption experiments were performed by using several alkanes (pentane, hexane, heptane, and octane), aromatic compounds (benzene, toluene, and xylene), alcohols (methanol, ethanol, propanol and butanol) and petroleum products (petrol, kerosene and diesel). The results showed the adsorption capacities of between 9 to 21 g per gram of dry aerogel. The adsorption capacities were dependent upon the surface tension and the density of the organic liquid. By increasing the surface tension and density of liquids the mass of adsorbed organic liquid increased. The desorption experiments included exposing the as-

adsorbed aerogel samples to the different temperatures and observing the variations in the weight until all the adsorbed organic liquid was removed. The rate of desorption increased with an increase in the temperature. Desorption was faster for organic liquids with smaller surface tension and larger vapor pressure. The transmission electron micrograph imaging (TEM) revealed that solvent adsorption did not cause a significant effect on the aerogel structure, whereas for the petroleum oils the shrinkage of about 50% in the aerogel network resulted in a dense structure after desorption. But in either case, the hydrophobicity was preserved so that the aerogel could be reused for adsorption. The further experiments resulted in reuse 3 times with no adverse change in the aerogel structure.

Wang (2011) reported the adsorption capacity of silica aerogel for vegetable oil, motor oil, and light crude oil as 15, 14 and 11 g/g aerogel respectively. According to the high affinity of aerogel, it may be considered as a good adsorbent for a variety of hydrocarbon contaminants. Wang et al. (2010) applied surface-modified silica aerogels in an inverse fluidization mode to remove vegetable oil from a dilute oil-in-water emulsion (1000 ppm COD or less). The emulsion stabilized by surfactant Tween 80 with the concentrations of 1 to 4 volumetric percent of the amount of added oil. The results showed that aerogel granules could adsorb about 2.8 times their weight of oil.

Wang (2011) and Wang et al. (2011a) used surface-treated silica aerogels in a packed and fluidized bed column to investigate the adsorption of various hydrocarbon contaminants from water. They studied the removal of six VOCs (benzene, toluene, chlorobenzene, trichloroethylene, *p*-xylene, and *o*-xylene) from aqueous and gaseous phase; as well as three different oils (vegetable oil, motor oil, and crude oil) dispersed in the water. The results showed that the adsorption of hydrocarbons from the gas phase occurred at the lowest rate, in comparison to aqueous and free phases. The rate of adsorption from an aqueous mixture was 5-10 times slower than the adsorption from the pure organic phase. By decreasing the size of the hydrocarbon droplets in water the rate and capacity of adsorption decreased. Addition of surfactant resulted in a more stable oil-in-water dispersion and led to a lower adsorption rate and capacity.

In another study, Wang et al. (2011b) investigated the adsorption of toluene from water by applying packed and fluidized beds of modified silica aerogels. The silica aerogel could adsorb toluene by about 4% of its weight. The Freundlich isotherm could fit very closely with the batch adsorption data. Standeker et al. (2007) synthesized and applied monolith silica aerogels for

adsorption of organic compounds including toluene, benzene, ethylbenzene, xylene, chlorobenzene, chloroform, 1,2-dichloroethane, and trichloroethylene from water. The synthesized aerogel represented the adsorption capacity of 15 to 400 times more than granular activated carbon. The adsorption capacity remained the same even after 20 cycles of adsorption/desorption.

In another research, Standeker et al. (2009) investigated the synthesized silica aerogels for adsorption of four aromatic hydrocarbons including benzene, toluene, ethylbenzene and xylene (BTEX) form the waste gas streams. The adsorption capacity of aerogel was 3 to 10 times higher than activated carbon and retained almost untouched in at least for 14 repeated cycles of adsorption/desorption. Perdigoto et al. (2012) studied the behavior of silica aerogels in the adsorption of benzene, toluene, and phenol from aqueous solutions. The examined adsorption equilibrium data exhibited a good correlation with Langmuir and Freundlich isotherm models.

Love et al. (2005) modified the silica aerogels to enhance the organic selectivity of the surface. They reported that CF3 surfaced-modified aerogels with a ($CH_2CH_2CF_3$) group at the surface could adsorb dissolved organic species with an oil to water ratio of 100. In a study by Liu et al. (2009), two samples of silica aerogels were synthesized and modified via two different processes to introduce either hydrophobic or hydrophilic surface characteristics. The experiments were conducted for adsorption of rhodamine B and dieldrin representing respectively typical soluble and slightly soluble organic compounds. The results showed that the hydrophilic silica aerogel had more affinity for adsorption of soluble compounds from aqueous solutions (rhodamine B), whereas hydrophobic silica aerogel had a high adsorption capacity on slightly soluble organic compound, dieldrin. Silica aerogel showed a stable adsorption capacity after 5 adsorption/desorption cycles.

Hrubesh et al. (2001) fabricated and used hydrophobic silica aerogels for removing toluene, ethanol, chlorobenzene, and trichloroethylene from water. The results exhibited that for all four organic solvents, the adsorption capacity of aerogel was larger than activated carbon. The ratio of adsorption capacity for aerogel in comparison to activated carbon was about 30 for low molecular weight, highly water-soluble solvents, and about 130 for immiscible solvents.

Gorle at al. (2009) used surface-modified hydrophobic and hydrophilic silica aerogels to investigate the aerogel behavior in the adsorption and thermal desorption of two highly volatile compounds, 1-menthol, and 2-methoxy pyrazine, dissolved in the gaseous CO_2 as a carrier. They

concluded that desorption temperature can be tuned by the change in the hydrophilic and hydrophobic content of aerogel. Also, the results showed that volatile compounds can be stabilized in the matrix of silica aerogels even in very high temperatures up to several hundred degrees of Celsius. For instance, about 50% of mass of tested organic compounds remained inside the hydrophilic aerogel network at temperatures about 250 to 300 °C. Hydrocarbons were stripped from the hydrophobic silica aerogel in the temperatures about 100-150 °C and lower.

Qin et al. (2013) fabricated silica aerogel and applied in the studies on the adsorption of phenol from dilute solutions in water (200 mg/l). They reported that the Freundlich isotherm can represent the equilibrium data. In addition to the application for uptake of organic contaminants, aerogels have been investigated to remove heavy metals from solutions as well.

Shokouki et al. (2010) synthesized and modified silica aerogels and applied them for heavy metal removal. Aerogel showed a capacity of adsorption for Cd^{2+}, Ni^{2+}, Pb^{2+} and Zn^{2+} cations from aqueous solutions as large as 35.71, 40.00, 45.45 and 34.48 milligrams per gram of aerogel, respectively. All aforementioned studies have been focused on the application of aerogel on the removal of organic and inorganic contaminants from aqueous and in a few studies, gaseous environments.

2.5. Desorption of Contaminants

Sorption plays a highly important role in the fate and transport of materials on the planet. With the same degree of importance, desorption takes place simultaneously and concurrently in the natural environment. Pollutants adsorb onto and desorb from a solid phase. For instance, spilled hydrocarbons already diffused into the soil matrix, stuck inside the oil sands tailings or attached to the sediments gradually are emitted into the soil, air, and water over time (Kan et al., 1994). For decades, natural sorption and desorption of contaminants and their application in the environmental cleanup have been studied. In this section, the occurrence of desorption and its influence on the material cycles in natural environments and environmental operations is briefly discussed.

Agitated washing is a common *ex-situ* method for remediation of contaminated soils and sediments. Solvent extraction accompanied with vigorous mixing is a well-known method for

measurement of hydrocarbon contaminants in the solid media. Applying enhanced mechanical decontamination reduces the amounts of chemical substances added to the natural environmental solid media. Mechanical decontamination can eliminate the need for applying heat and high-temperature technology and can be applied in situ or *ex-situ*, based on the availability of land and costs. Fluidized bed reactors, slurry reactors, ultrasound and cavitation reactors, attrition and jet pump scrubbers have their own limitations. If not treated, desorbed pollutants may transfer and spread in the surrounding environment and finally enter the food chain.

It is believed that up to 90% of the contaminants are adsorbed onto the fine particles as a segment of a larger cluster of soil or sediment. The attrition scrubbers use a mixer impeller or metallic balls to wipe off the outer layer of contaminated solid particles. Attrition efficiency for contamination removal depends on the extent of produced fine particles (Bayley & Biggs, 2005a; Jobin et al., 2015; Petavy et al., 2009a; Petavy et al., 2009b; Schaaff et al. 2004; Strazisar & Seselj, 1999). Jet pump scrubbers are accelerated attrition reactors substituting the mixer impeller with a strong liquid jet in order to reduce the contamination content in soils and sediments. Applying a high-speed jet beside the attrition phenomenon creates cavitation and enhances the destruction and oxidation of the contaminants (Bayley & Biggs, 2005b; Bayley & Biggs, 2006a; Bayley & Biggs, 2006b). Fluidized bed solid-liquid or solid-gas reactors generate a high rate of mass transfer between an agitated floating solid and an upward stream of liquid or gas (Arrar, 2007).

2.5.1. Natural Desorption in the Environment

Natural desorption is an ongoing phenomenon in the environment. Desorption may accompany the sorption process (Chai et al., 2006; Haddadi et al., 2009; Huesemann et al., 2006, Stone & O'Shaughnessy, 2005). The contaminants continuously diffuse from the sediments into the water bodies (van Noort et al., 2003). The soil gradually emits the contamination into the air and groundwater (Johnsen & Karlson, 2007).

During desorption, the bonding between the contaminant and the solid phase breaks and the molecule of the contaminant detaches from the solid phase. Natural desorption is affected by the existence of many factors such as concentration gradient (chemical potential), vortices in the surrounding environment, sunlight and variations in the temperature, pH, salinity and ionic strength, redox potential, oxidation and chemical transformation, the composition of solid media,

gravity, capillary forces, solid particle size, rate of diffusion, enzymes or other biological products, aging and the contact time (Abolfazlzadehdoshanbehbazari et al., 2013; Hiller et al., 2009; Paraskewhich, 2008; Wu & Sun, 2010; Xu et al., 2008).

The slow process of natural desorption can be accelerated by a variety of natural or man-made stimulators. For instance, after a heavy rainfall in a city water runoff carries the soil and dust on the ground surface towards the drainage system (Dong et al., 2013, Gan et al., 2005). In the same way, during a flood event, the disturbance in the water causes resuspension of sediments at the bottom of a river forming a sediment-water slurry (Smit et al., 2008 & 2010).

Resuspension may be formed by other natural events, such as tidal currents, strong winds, and storms, heavy rainfalls and biological activities. As well, anthropogenic perturbations such as dredging, oil extraction, and trawling may cause resuspension (Tengberg et al., 2003). Resuspension stimulates desorption of organic and inorganic chemical species from the sediment (Smit et al., 2008 & 2010). Because of its importance, the desorption of the contaminants during resuspension has received attention by environmental researchers. Particularly, the kinetics of desorption and prediction models have been investigated extensively.

Birdwell et al. (2007) reviewed the research literature about desorption kinetics of hydrophobic organic substances from the sediment during the resuspension. Fojut & Young (2011) investigated desorption of four pyrethroid insecticides from the suspended solids in the irrigation runoff water. They found that the properties of the sorbent had the highest effect on the desorption rate. Also, a higher content of the organic carbon resulted in a lower desorption rate. Yang et al. (2008) studied the effect of resuspension on the release of 16 polycyclic aromatic hydrocarbons (PAHs) from the river sediments. They applied the input energy levels (shear stress) of 0.2 and 0.5 N/m^2, as typical energy levels present in the many tidally-driven aquatic bodies. They found that after 15 minutes of resuspension, PAHs were released on average at 42% of their initial concentrations. The higher energy level caused a higher rate of desorption. Also, they observed that the low molecular weight PAHs (2 or 3-ring) were released faster than median molecular weight (4-ring) PAHs.

Based on the experiments by Feng et al. (2007) the remobilization of polycyclic aromatic hydrocarbons is highly dependent on the magnitude of shear stress. Cantwell & Burgess (2004) showed that during the resuspension period the concentrations of heavy metals in the sediment particulate and aqueous phase fluctuate. The concentration fluctuation was the highest for

cadmium and nickel. In a series of experiments performed by Latimer et al. (1999), the mobilization of polychlorinated biphenyls (PCBs) and PAHs in the resuspension events was investigated. The results indicated that during a resuspension event desorption and distribution of the contaminants is dependent on the chemical composition and textural characteristics of the sediment as well as the winnowing regime.

Cantwell et al. (2008) evaluated the prediction models for the release of heavy metals (Cd, Cu, Hg, Ni, Pb, and Zn) from the sediments stimulated by resuspension. The experimental concentrations of released species were lower than the predicted values by mathematical models. A series of experiments were conducted by Kalnejais et al. (2010) on the release of nutrients and metals (Ag, Cu, Fe, Mn, and Pb) from the sediments during resuspension. The results revealed that during the disturbance, the magnitude of shear stress has a high degree of importance. In the input shear stresses below the erosion threshold the release of solutes was limited; while by increasing the shear stress to beyond the erosion threshold, the concentration increased by raising the shear stress. The magnitude of release was higher than could be attributed to the regular mixing of pore water into the surrounding bulk liquid.

A new approach to the improvement of the quality of a water-sediment system by applying a man-made resuspension event has been investigated by Fukue et al. (2012). The method included the suspension of the sediment by an air-water jet, pumping the slurry to a tank, filtration, and disposal of the solids. By applying this procedure, the chemical oxygen demand (COD) was reduced by 95%, total phosphorous by 50%, total nitrogen by 100% and sulfide by 75%. At the same time, the aeration of sediments created an aerobic environment to facilitate the decomposition of the organic pollutants. According to Mulligan et al. (2009), resuspension can be created by similar techniques such as stirrers, as well. For anaerobic sediments, aeration creates an aerobic environment and enhances the oxidation or destruction of the contaminants.

2.5.2. Enhanced Desorption in Environmental Remediation

The slow natural pace of the contaminant desorption can be beneficially accelerated to decontaminate the solid media. Chemical, physical and biological stimulators cause a rupture in some of the contaminant-solid bonds. The rupture can occur in an enhanced desorption event caused by a solvent with a high affinity and solubility. A solvent can dissolve the contaminant and

extract it from the solid matrix. Detergents and surface-active agents enhance the detachment of the contaminants. Raising the temperature or decreasing the pressure facilitates evaporation of the contaminant. Microorganisms or some of their products, e.g. enzymes and biosurfactants, can loosen or destroy the solid-contaminant bonding. And at last but not the least, applying mechanical forces by vigorous agitation in the form of impact or shear can separate the contaminant from the solid matrix. Agitation can be created by a mixer in a slurry reactor, an attrition scrubber, a liquid jet or a fluidized bed reactor. As well, the cavitation at the surface of a solid phase can create an enormous impact shock, a highly raised temperature and a low pressure simultaneously. The cavitation can be generated by applying ultrasound or a strong fluid jet. Following, the important methods of enhanced desorption connected to the present research are discussed.

In the slurry reactors and continuous stirred-tank reactors the solute transfers from the solid to the bulk of liquid due to the existence of turbulence (Puskas et al., 1995). The bioslurry reactors operate based on the increased mass transfer of the contaminants and other substrates towards the submerged microorganisms in a mixing pattern (Zappi et al., 1995). Similarly, ultrasound is a well-known mean for extraction of hydrocarbons from solid media in laboratory extractions (Mahamuni & Adewuyi, 2010). Cavitation is the formation of bubbles in a liquid due to lowering the pressure or imposing a high extent of energy. The cavitation can be formed by imposing ultrasonic waves (ultrasound cavitation) or in high-speed liquid flows in jet reactors (hydrodynamic cavitation). The cavitation has been investigated for disinfection of water and decontamination of soil and sediments (Meuzle et al., 2009; Ozonek, 2012; Petkovsek et al., 2013; Sawant et al, 2008; Shah et al., 1999). Lately, cavitation has been studied for the extraction of bitumen from oil sands (Bukharin, 2011, Bukharin et al., 2012).

2.5.3. Soil and Sediment Washing

The washing process, also sometimes known as leaching or flushing, includes flowing water or a solution through a solid media to gradually remove the contaminants. The washing operation removes a wide range of contaminants from solid by physical and or chemical means. Most of the organic contaminants such as PAHs, PCBs, TPHs, halogenated solvents, chlorinated phenols and inorganic contaminants such as heavy metals and cyanides can be removed by the washing technique. For potentially soluble species, e.g. metallic ions, the solution dissolves the contaminant

and removes it from the solid matrix. For washing organic and petroleum hydrocarbons it is assumed that though these contaminants are not very soluble, they are not completely insoluble in the aqueous phases. Washing has been commercially used or studied for decades. The soil washing and the other low-temperature techniques are commercially applied when the contamination in solid media exist in a low concentration. Harsher methods such as thermal desorption or chemical extractions are applied for intermediate levels of the contamination. Fluidized beds, rotary kilns, and plasma torch are utilized for the highly-contaminated solid media (Cole, 1994; ICS-UNIDO, 2007; Mulligan et al., 2009).

The washing process is more effective on the coarse particles rather than fine ones. To enhance the efficiency, the hot water is used or detergents, surfactants, biosurfactants, organic solvents, chelating compounds, acids, and bases are added. A higher temperature increases the solubility of contaminants, raises the kinetic energy (diffusibility) of water molecules and reduces the viscosity of hydrocarbons, leading to a higher performance. In a successful washing process design, it is important to have enough information about the mineralogy of the solid media. Washing is feasible for reducible oxides, carbonates, organic and exchangeable fractions. Washing the contaminants which are residually bound to the solid media is difficult and not cost-effective. Washed soils or sediments need to be dewatered.

Washing is cost-effective for small and relatively small volumes of the contaminated solid, particularly when the costs of disposal are high. The used solutions possibly have to undergo a further treatment, particularly if the effluent contains high concentrations of hazardous substances. The effluent may emit hydrocarbons to the air. Washing may not be effective on fine particles such as clays and silts. Then extraction by a solvent or CO_2 can be considered as an effective option. Due to adverse consequences, washing is taken in account if the other methods are not feasible (Cole, 1994; ICS-UNIDO, 2007; Mulligan et al., 2001b & 2001c & 2001d & 2009). Washing is a slow technique but eventually, the solid media becomes relatively clean. Important parameters controlling the solid washing process include (Cole, 1994)

- the porosity of the solid phase
- the partition coefficient of pollutant for solid-water distribution
- the strength of binding forces between the contaminant
- the temperature of the aqueous phase.

Mechanical methods, involving an intensive micro- or macro-agitation, enhance the efficiency of soil washing (Feng et al., 2001; Weber & Kim, 2005). The same concept has been applied for extraction of the contaminants, particularly hydrocarbons, in the laboratory measurements in research or reference protocols (Schwab et al., 1999). Mechanical treatment techniques fall under several categories. The following sub-sections discuss those techniques.

2.5.4. Slurry Reactors: Three-phase Agitated Tanks

A slurry reactor is a multi-phase agitated tank containing a suspension of liquid and solid particles. As the reactor is not working at full capacity, a gas phase as the third phase exists at the top of the liquid. Slurry reactors are suitable when a high rate of mass transfer is required. In addition, due to their simple design, fabrication process, operation, and control, they are one of the most common types of solid-liquid reactors in the research and industry. Slurry reactors are applied in the soil washing commercially (Inglezakis & Poulopoulos, 2006). (ICS-UNIDO, 2007; Mulligan et al., 2009; Robles-Gonzalez et al., 2008). Fluid dynamics and mass transfer phenomena in the solid-liquid systems have been the subject of many studies (McCabe et al., 1993; Perry & Green, 1999; Treybal, 1980).

Diluted slurries are formulated similar to clear liquids, while concentrated slurries may behave like a non-Newtonian fluid (Treybal, 1980). Ahn et al. (2008) studied the mass transfer of polycyclic aromatic hydrocarbons (PAHs) in the slurries of contaminated soil and sediments. They applied activated carbon, coke breeze, polyoxymethylene as amending sorbents to investigate the mass transfer and intra-particle diffusion phenomena in the dense slurries of heavy oil or tar sludge. They used a kinetic partitioning model to simulate the solid-contaminant interactions. They concluded that PAHs from the heavy oil were detached from the solid in the form of small droplets. Activated carbon particles in the slurry quickly sequestered the secreted oil. Coke breeze was considerably slower than activated carbon. The presence of activated carbon hindered polyoxymethylene pellets to adsorb the oil. The rate of adsorption by the strong adsorbent was considerably higher than the rate of regular biodegradation.

Smith et al. (2008 & 2010) designed a slurry reactor, called Solid Phase Extraction with External Desorption (SPEED), to study the desorption mass transfer of organic compounds similar to the persistent organic pollutants in a simulated flood event from soils and sediments. They reported

that for the fine particles (10 μm) the equilibrium for distribution of the contaminant in the solid-water system was rapidly reached. For the larger particles (84 μm), such an equilibrium was slow. The desorption was constrained by the intra-particle diffusion. They concluded that in a disturbed slurry system, the particle size distribution and the hydraulic retention time control the desorption rate. Kim and Weber (Kim & Weber, 2005; Weber & Kim, 2005) studied the effect of mechanical mixing, corresponding power consumption, and rheology on the desorption of contaminants in the dense slurry systems. They used sorbent slurries with 57-67% (w/w) solids to form a non-Newtonian (pseudo-plastic) fluid in which apparent viscosities varies with the shear rate. They reported that the rates of release of phenanthrene were highly dependent on the association with the sorbent organic matter. The fraction of phenanthrene associated with rapidly desorbing sorbent organic matter was very responsive to the relatively slow auger mixing. The fraction of phenanthrene associated with slowly desorbing or resistant sorbent organic matter did not represent any significant increase in the desorption under auger mixing. The unaffected rate of desorption was attributed to the limited intra-particle diffusion processes which are not accelerated by the laminar mixing.

2.5.5. Mechanochemical Treatment

A number of organic contaminants have been successfully remediated through the mechanically induced reactions by ball milling. Sulfonic acids, hexabromobenzene, PCBs and other organo-halogenated compounds have been degraded by this technique. Based on a study, the organic contaminants were degraded via either slow conversion mechanisms or combustion-like reactions occurring after an induction period in a very short time. The slow transformation of organic substances occurred due to the increasing the defects in the solid matrix resulting in a gradual degradation of the organic contaminant. In the combustion-like reactions, the high temperatures caused exothermic reactions in the relatively short times leading to the destruction of the organic molecules (Caschili et al., 2006; Concas et al., 2007). A study on the deployment of the same method for immobilization of Cd, Pb, and Zn in the soil revealed that the efficiency was directly dependent on the ball milling time. Milling caused a slight amorphization in the soil and a decrease in particle size. After 3 to 7 hours of milling, the leachable fraction of heavy metals decreased under the USEPA regulatory limits (Concas et al., 2007). Also, Montinaro et al. (2007, 2008 &

2009) immobilized cadmium, lead, and zinc by applying this technique without significant alteration of the soil matrix.

2.5.6. Attrition Scrubber

It is shown that the main portion of the contaminants, up to 90%, is adsorbed on to the fine particles. These fine particles may be free or attached on the surface of a larger soil or sediment cluster. An attrition scrubber applies the mechanical impact and shear force to scratch and wipe off the outer layer of the contaminated particles. Blade mixers or metallic balls conduct the attrition process. Attrition efficiency depends on the extent of the produced fine particles (Bayley & Biggs, 2005a; Jobin et al., 2015; Neesse et al., 2004; Strazisar & Seselj, 1999). The conventional wet attrition process can achieve a fine particle production of only 1-2% of the total particles with a diameter less than 5μm (Schaaff et al., 2004). The attrition scrubber is considered a physical separation technique similar to screening, sedimentation, centrifugation, hydrocyclones and flocculation (Mulligan et al., 2009). Petavy et al. (2009a, b) evaluated the application of attrition scrubbing in the decontamination of stormwater sediments. They reported that after attrition and separation, up to 70% of stormwater sediment could be reused.

2.5.7. Cavitational Remediation

Cavitation is a phenomenon in which gas or vapor bubbles are produced and collapsed due to a dramatic static pressure drop, impact of high energy waves or introduction of high amounts of energy to a small volume of liquid. The sharp reduction in the pressure is a regular occurrence on the edge of the mixer blades or marine vehicle impellers when the linear speed of the blade exceeds a certain level (hydrodynamic cavitation). Cavitation due to the high-energy waves may form by an ultrasound source (acoustic cavitation). Discharge of a high-energy density into a small volume of liquid can be generated by a laser (optic cavitation) or proton beam (particle cavitation) leading to the cavitation. Formation and collapse of the bubbles near the solid surface produces extremely strong liquid micro-jets and shock waves. It causes inter-particle collisions, highly raised temperature and extremely low pressure and low concentration zones simultaneously in a micro-

scale. This extreme micro-environment leads to the erosion of the solid surface, detachment of fine particles, evaporation, destruction, and desorption of the contaminants (Shah et al., 1999).

Numerous studies have been focused on the exploitation of the cavitation in environmental engineering. The cavitational remediation methods are among the advanced oxidation processes, AOPs. The cavitational reactions trigger chemical conversion in the molecule of contaminant. The hydroxyl radical (·OH) produced during the cavitation accelerates the oxidative destruction of the contaminants (Ozonek, 2012; Shah et al., 1999). Petkovsek et al. (2013) by utilizing a rotation generator of hydrodynamic cavitation combined with hydrogen peroxide achieved up to 80% of removal of pharmaceuticals (diclofenac, ibuprofen, carbamazepine, and ketoprofen) from water. Sawant et al. (2008) investigated the effect of hydrodynamic cavitation on the disinfection of water from zooplankton in the sea water. The result showed that the cavitation and turbulent fluid shear killed more than 80% of the zooplankton population.

Fukue et al. (2012) successfully applied cavitation for removal of fine particles and organic matters from sediments. They concluded that cavitation is more efficient than water jets. Badve et al. (2013) applied the hydrodynamic cavitation generated by a stator and rotor reactor for treatment of a wastewater from wood finishing industry containing high concentrations of volatile organic compounds. They reported that the COD removal was dependent on the speed of the rotor up to a certain level. As well, the longer residence time of the wastewater resulted in the higher rate of degradation up to an optimum value. At the 1800 rpm, cavitational yield (measured by COD reduction, mg per total energy supplied, J) was the highest but resulted in not the highest COD reduction of 42%. At the rotational speed of 2200 rpm, the reduction in COD was 49%.

In a study by Jyoti & Pandit (2001), the effectiveness of the cavitation as a microbicide technique was investigated. The results indicated that hydrodynamic cavitation was an economical and energy-efficient method compared to the conventional non-chemical water treatment techniques. Degradation of benzene, toluene, ethylbenzene and xylenes, BTEX (Brautigam et al., 2009), alachlor (Wang & Zhang, 2009), methyl parathion (Patil & Cogate, 2012), p-nitrophenol (Capocelli et al., 2014), dichlorvos (Joshi & Cogate, 2012), chitosan (Wu et al., 2014) and Red 120 dye (Saharan et al., 2011) are among instances of research on the cavitational degradation. Up to now, due to the costs of technology and energy, the cavitational remediation is not cost-effective (Shah et al., 1999). Bukharin (2011), and Bukharin et al., (2012) applied the cavitation for

extraction of bitumen from oil sands. They reported that cavitation can eliminate the need of application of hot water providing the same efficiency in oil extraction.

2.5.8. Ultrasound

High frequencies of sound waves have enormous capabilities in the different fields of science and technology. Application of the ultrasound in environmental science has been researched for decades (Sillanpää, 2011). Ultrasound is one of the most common techniques for formation of the cavitation in a liquid. In the ultrasonic cavitation, micro-bubbles are formed, grow, and finally collapse. Collapsing the bubbles creates high pressure hot spots of 5000°C and 50,000 kPa in extremely short periods of few microseconds. The shock waves of bubble collapse cause inter-particle collisions (Mulligan et al., 2009). Even in the absence of cavitation, ultrasound waves can generate a large amount of energy enough to create a large momentum to desorb the contaminants (Sillanpaa, 2011).

In an environmental solid media, the ultrasound increases the porosity of the solid media and facilitates the diffusion of the flow through the solid matrix resulting in desorption of the contaminants. It is believed that the mechanism of desorption of the organic contaminants from the solid media includes three important factors: a) creation of very high temperature zones resulting in breakage of physical bonding between the contaminant and the solid; b) formation of high speed micro-jets and high pressure shock waves wiping off the contaminant; and c) formation of acoustic micro-streaming vortices on the surface of the solid media and inside the pore matrix (Sillanpaa, 2011).

Experiments in the laboratory have shown that the ultrasound waves stimulate the production of hydroxyl ions (·OH) and accelerate the oxidation of the contaminants. A study on the remediation of heavy metals from the dredged contaminated sediments showed a maximum of 83% removal in 90 minutes. Ultrasound can stimulate the destruction of organic pollutants due to the thermal decomposition and formation of oxidants (Sillanpää, 2011). Laboratory experiments resulted in more than 98% removal for polycyclic aromatic hydrocarbons (PAHs) and 95% for removal of chromium (Mulligan et al., 2009). Diesel, total petroleum hydrocarbons and persistent organic pollutants (POPs) such as hexachlorobenzene, phenanthrene, DDT, atrazine, endosulfan, lindane, simazine, tetrachloronaphthalene have been remediated in soils and sediments by the ultrasound

technique. In sonochemical methods, ultrasound is deployed to enhance degradation of the contaminants by chemical processes e.g. using hydrogen peroxide (Feng & Aldrich, 2000, Mulligan et al., 2009; Sillanpää, 2011). Due to high costs and difficulties in scale-up, ultrasound has not been commercialized in large scale remediation (Mahamuni & Adewuyi, 2010).

2.5.9. Jet Scrubbers

Jet reactors, also known as venturi scrubbers and jet pump scrubbers, work in a similar way to the attrition scrubbers. They remove the fine particles attached to the surface of larger particles of soil and sediments in a slurry medium; whereas in jet scrubbers a high-speed flow of fluid functions similar to the blades in an attrition reactor. By increasing the flow rate of fluid passing through a narrow venturi, the static pressure decreases. When the pressure is enough low to approach the vapor pressure of the liquid at the same temperature, the liquid begins to boil and consequently, cavitation occurs. Therefore, based on the speed of the flow in jet reactors, the attrition can be accompanied by cavitation. Jet scrubbers have been investigated for disinfection of gram-negative and gram-positive bacteria, as well as remediation of various contaminants e.g. dewaxed petroleum-based hydrocarbons, diesel range hydrocarbons (C11-C20), crude oil and mineral oil in the soil and sediments (Bayley & Biggs, 2005b & 2006a & 2006b; Feng et al., 2001; Loraine et al., 2012).

2.5.10. Fluidized Bed Reactor

Fluidization is described as passing a fluid, gas or liquid, through a bulk of granular solid material at high enough velocities to suspend the solid particles. High rates of mass and heat transfer during fluidization makes the phenomenon attractive to be deployed in the chemical and environmental unit operations. Theory of fluidization and fluidized reactors in both solid-gas and solid-liquid modes have been developed over the decades (McCabe et al., 1993; Perry & Green, 1999; Treybal, 1980). Fluidized bed reactors have been applied and investigated for the treatment of the soil, sands, and sediments contaminated with a wide range of hazardous substances such as diesel fuel (Arrar et al., 2007), light and heavy oil (Alappat et al., 2007) and petroleum (Lee et al. 1998).

Fluidized beds are also used for the size-based particle separation (Mulligan et al., 2001a, 2001c & 2009).

2.6. Desorption-Sorption Method

The recovery methods for submerged oil spills are expensive, complicated and not very efficient (Fingas, 2011). Mechanical forces facilitate washing the contaminants from the solid media (Khan et al., 2004; Schwab et al., 1999). Mechanical remediation methods eliminate or minimize the need for the addition of washing agents.

On the other hand, recently, aerogels, due to their physical and chemical properties such as high adsorption capacity, exceptionally lightweight, high porosity, strong chemical affinity, and harmlessness can be considered as reliable substitutions for conventional sorbents. Silica aerogels are nontoxic and strongly hydrophobic (Norris & Shrinhasan, 2005). There are only a few studies on silica aerogels for contaminant removal from water and air. (Korhonen et al., 2011; Parale et al., 2011; Reynolds et al., 2001a & 2001b; Standeker et al., 2007; Standeker et al., 2009; Venkateswara Rao et al., 2007).

There is a gap in the studies on the application of a combined turbulence-sorption mechanism in a closed-loop system for remediation of solid media. Utilizing a closed physical-mechanical system for contamination removal from the solid media seems attractive. Applying a regular high-speed mixer, instead of a water-jet ejector or an ultrasonic horn, eliminates the need for a sophisticated control mechanism, reduces scale-up difficulties and avoids costly remediation facilities. Design of an ordinary mixing system, where there is enough knowledge and experience, is more convenient than a jet cavitation or an ultrasound generator. Furthermore, exploiting aerogels can reduce the release of pollutants into the environment. Accompanied by physical forces, aeration of the solid media generates a highly aerobic condition and enhances the decomposition of pollutants.

2.7. Chapter Overview

Hydrophobic organic pollutants are recognized by high toxicity, slow rate of degradation and wide spreading in the environment. A major part of pollution in the water bodies sorbs onto the sediments lying at the bottom. The concentrations of pollutants in the sediments are higher than the contacting water by orders of magnitude. Mechanical remediation methods eliminate or minimize the necessity of addition of washing agents such as detergents and surfactants. Slurry reactors, mechanochemical treatment, attrition scrubbers, cavitational remediation, ultrasound, jet scrubbers, and fluidized bed reactors are considered as mechanical remediation techniques. For the environmental operations, conventional mechanical methods are either energy-consuming, time-consuming, cost-ineffective, sophisticated to control, difficult to scale-up or of low efficiency. In addition, in many cases, the produced effluent contains high concentrations of contaminants with a need for further treatment before returning to the environment.

On the other hand, sorption is one of the key remediation technologies in the present and future. Sorbents are an important means in the oil spill cleanup operations. Silica aerogels could be a potential alternative for activated carbons. Aerogels, due to their physical and chemical properties such as high adsorption capacity, exceptionally lightweight, high porosity, strong chemical affinity, and harmlessness can be considered as reliable substitutions for conventional sorbents. Modified silica aerogels are nontoxic and strongly hydrophobic. In this research, the combination of desorption-sorption has been applied to enhance the detachment of hydrocarbon contaminants from sediments and separate them from the sediment-in-water slurry by sorption by hydrophobic aerogels.

Chapter 3 – Experimental Methods and Methodology

3.1. Enhanced Desorption-Sorption Setup

3.1.1. Series of Preliminary Configurations

To have some preliminary idea about the optimum flow rate of the slurry, gas hold up, the retention time for liquid-gas separation and the best slurry-aerogel contact method, a series of smaller temporary setups with 27 different bench-top configurations were built and experiments were carried out. The tray contactor, basket contactor, packed bed, fluidized bed, moving bed, bubble column, internal-loop, external-loop, and slurry reactors were among the configurations.

3.1.2. Desorption-Sorption Setup

Based on the data collected from the preliminary setups, the main process setup was designed and built as the optimum design for conducting the experiments. The setup included a forced desorption (vigorously agitated) vessel, a gas-liquid separation chamber, an adsorption (aerogel) column, pump, two-range flow meters and a control panel (Figures 3.1 and 3.2).

The turbulence chamber was utilized as a desorption stimulator to accelerate the detachment of contaminants from the solid media. The adsorption column was made of a glass tube with 4.9 cm internal diameter and up to 25 cm length. The arrangement of piping allowed the slurry stream to flow into the column upward or downward. A sampling port and a purge port were implemented

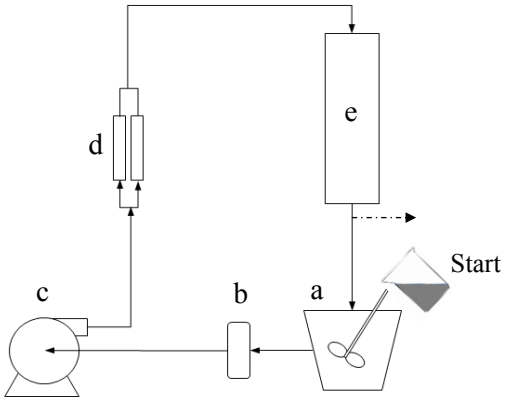


Figure 3.1. Main setup including the (a) agitation vessel, (b) liquid-gas separation chamber, (c) pump, (d) flow meters and (e) adsorption column

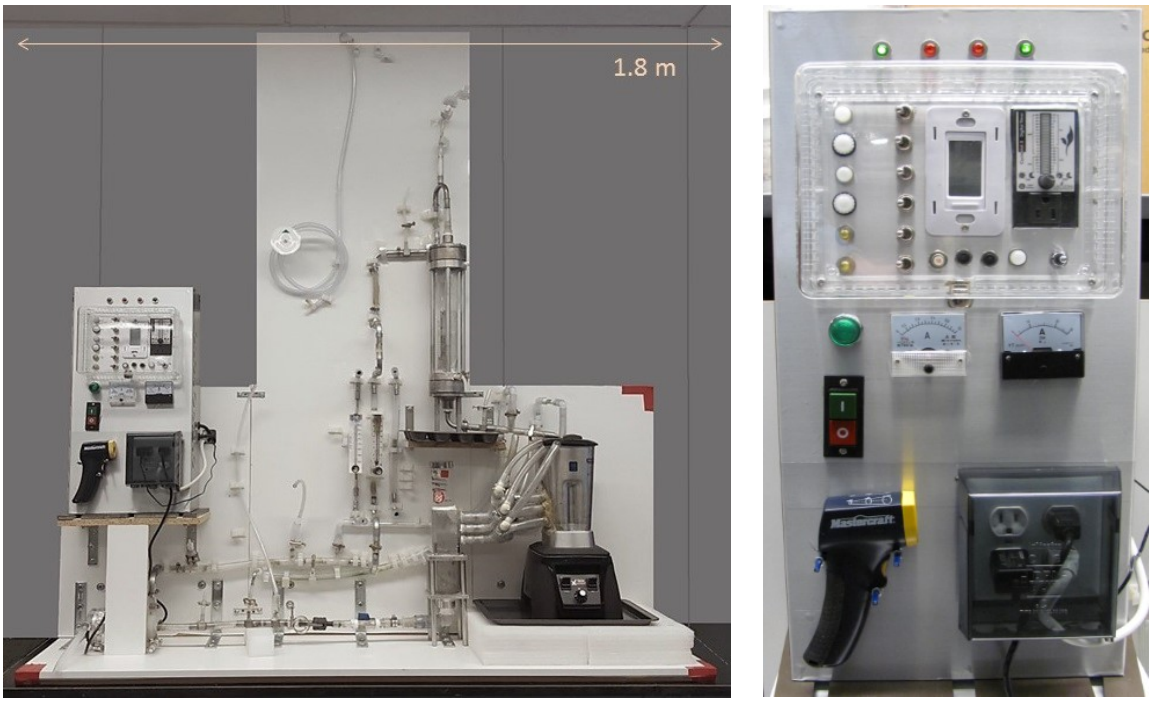


Figure 3.2. The desorption-sorption setup: the process setup (left) and the control system (right)

for sampling and working in a semi-batch configuration. Two relief valves allowed the release of the small bubbles of air from the column. Hydrophobic surface-modified silica aerogel was used as a typical adsorbent to adsorb and sink the contamination. The arrangement of several bypasses and 22 valve streams could enable experiments in different flow directions, flow rates and contact times.

During the preliminary experiments, it was revealed that submerged aerogel granules strongly repel the water and tend to have a layer of air around them. Therefore, a special mechanism and several air bubble traps were placed in the system to ensure that the inlet slurry to the adsorption column does not have visible and large air bubbles. To minimize the loss originated from the adsorption or leaching of hydrocarbons by the exposed wall surfaces, a Teflon pump, and Teflon-lined tubing was used. The agitation vessel was made from stainless steel 316 which is one the best-suggested materials for hydrocarbon laboratory tests. The adsorption column and separation chamber were made from glass. The tubing joints were made from Teflon or stainless steel 316. A control system was designed and built to control the agitation vessel and pump and ensure the safety of the personnel and system simultaneously. As the agitator rotated in speeds of higher than 10000 rpm, to avoid the overheating the motor, a cyclic timer was installed on the control panel to turn ON/OFF the agitator intermittently. The time intervals were adjusted for 20 seconds ON and 60 seconds OFF. The flow rate of the slurry entering to the column could be adjusted by a series of valves which enabled recycle of the stream, two liquid flow meters (high range 0.95-9.5 l/min and low range 0.1-1.5 l/min) and an electrical pump controller on the control panel. A main stream of water from tap water was installed to wash inside the whole setup after every experiment. The electrical current passing through the agitator and pump was indicated by two ampere meters on the board. During the experiments, the temperature of the agitator, pump electromotor and other parts could be measured by a remote laser thermometer (model Mastercraft, temperature range: -20 to 315^{o}C). A cooling water coil was installed around the pump to prevent overheating. A series of circuit-breakers were embedded in the control panel for safety. The system could be shut down by a main emergency switch in the case of an incident.

3.1.3. Processing of the Sediment

For processing the sediment, the following steps were followed (Figure 3.3):

1. The setup pre-washed by tap water was drained.
2. 3 g of aerogel were placed in the adsorption column.
3. To start the process, 2.5 liters of water were poured into the agitation vessel.

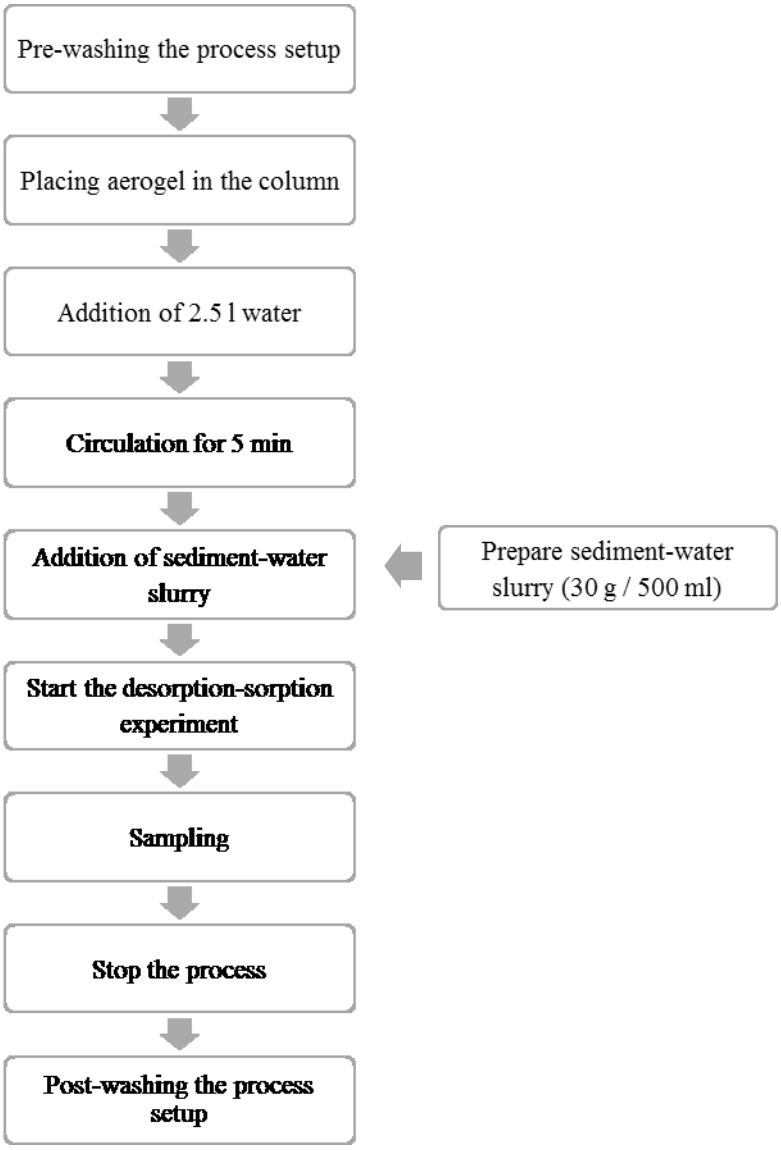


Figure 3.3. Procedure for running the desorption-sorption setup

4. The pump was started and the water was circulated in the system for about 5 minutes to make sure the system works stably and ensure there were no leaks.
5. A slurry of 30 g sediment in 500 ml of water was prepared.
6. To start the experiment the pre-made sediment-water slurry was poured into the agitation vessel and the time was registered by a stopwatch. Sediment samples were already homogenized and screened with a 1-mm mesh stainless steel strainer to make sure that there were no small pebbles inside to damage the pump and agitator blades.

7. The experiments were continued for 3 hours until the results showed there was no further significant desorption of hydrocarbon contaminant. As mentioned previously, to avoid overheating the agitator motor, it was turned ON and OFF by a cyclic timer as 20 seconds ON and 60 seconds OFF.
8. In pre-determined time intervals, slurry samples were taken from a sampling port.
9. After 3 hours the experiment was terminated. The process setup was turned OFF, drained and washed with tap water.

To distinguish between the effect of the adsorption and desorption mechanisms on the whole process, the desorption-sorption experiments were conducted in 4 different series: control (no agitation / no aerogel), only agitation, only aerogel (sorption) and the presence of both agitation and aerogel (sorption).

Also, to evaluate the natural leaching of the contaminants from the sediment, a series of experiments were conducted by placing pre-weighed samples of sediments in the water and measuring the change in concentration of hydrocarbon in both sediment and water. The adsorption characteristics of the aerogel were studied individually.

3.1.4. Sampling

In the pre-determined time intervals (0, 3, 30, 60, 120 and 180 min), 300 ml of sediment-in-water slurry were taken from the setup by a graduated cylinder and weighed by a laboratory balance. The slurry was divided into six 50-ml aluminum centrifuge tubes and centrifuged at 3700 rpm for 30 minutes. To avoid adsorption of tiny amounts of hydrocarbons on the wall, the conventional polyethylene centrifuge tubes were not used. The supernatant was separated carefully and collected for liquid-liquid extraction by hexane for further gas chromatographic (GC) analysis. 3.5 grams of magnesium sulfide were added to the wet sediment at the bottom of tubes to dry the solid and to remove it from the tubes. The coarse mixture of sediment and magnesium sulfate was weighed and ground to a fine powder with a handheld electrical grinder modified for small sediment samples. The powder was kept in a glass vial for extraction by hexane according to the standard protocol explained later. To consider the water content of the centrifuged and separated sediment

in the calculations, the water content measurement was conducted in 5 centrifuged samples and the average was recorded.

3.2. Sediment Samples

The sediments samples were collected from sector 103 of the Port of Montreal. Sector 103 is located on the northern coastline of the river and has been a ground for various industrial activities, particularly oil and metal refining, for over five decades. (Appendix I) (Alavi, 2011). The bottom of the bays in sector 103 of the Montreal port area was composed of a large quantity of contaminated sediments. These sediments were from the historic effluent discharge from the companies such as Noranda-CCR Refinery, Imperial Oil, Shell Canada, Gulf Canada (bought by Ultramar). Other contaminants passed through the sewage system of the city of Montreal East, which also led to sector 103. The contaminants include large oil and grease stacks and several heavy metals (copper, selenium, mercury, etc.). The average concentration of more than 12 contaminants exceeded the interim sediment quality criteria meaning that over 90% of the benthic organisms could be killed by their concentration (Forget & Lajeunesse, 2001). To minimize the inhomogeneity of the sediment samples, several kilograms of sediment were mixed completely and homogenized by hand and an electrical paste mixer. The homogenized samples were stored in a glass container in a fridge for further experiments.

3.3. Materials

3.3.1. Chemicals

Gas chromatography grade hexane Optima with a minimum purity of 99.9% was obtained from Fisher Scientific Canada. Anhydrous sodium sulfate ACS with 99% purity and 10/60 mesh for analysis, anhydrous magnesium sulfate with at least 99% purity for analysis and extra pure silica gel with 70-230 mesh were obtained from Fisher Scientific Canada.

3.3.2. Adsorbents

Granular aerogel type P300 was purchased from Cabot Co. (Figure 3.4). The surface of this type of aerogel is modified with tri-methyl-silyl groups ($-Si(CH_3)_3$) and is strongly hydrophobic. The properties of aerogel based on the producer's data sheet are represented in Table 3.1. The larger size of the aerogel granules (1.2 – 4 mm) in comparison to sediment particles (micrometer) allowed the sediments to pass easily through the aerogel bed and prevent clogging. The granular activated carbon used in this study was GAC 12X30, Siemens Water Technology Inc.

Figure 3.4. Granules of Cabot aerogel Type P300 aerogel used in this study (photo taken by the researcher)

Table 3.1. Properties of Cabot aerogel Type P300 (Cabot Inc.)

Property	Value
Particle density (kg/m^3)	120 - 180
Particle size range (mm)	1.2 - 4.0
Pore diameter (nm)	~ 20
Particle porosity (%)	90 - 95
Bulk porosity (%)	51
Surface area (m^2/g)	600 - 800
Surface chemistry	Fully hydrophobic

3.3.3. Gas Chromatography & Soil Calibration Standards

Soil and gas chromatography standards were purchased as listed below:

- The C10-C50 soil standard was purchased from the Quebec Expertise Environmental Analysis Center (Centre d'expertise en analyse environnementale du Québec).
- C10-C50 window solution: 50% weathered fuel no.#2 (Chromatographic Specialties Inc.)
- Retention time marker standard containing decane (C10), n-pentacosane (C25) and n-hexatriacontane (C36) (RESTEK)
- 5-α-androstane (Chromatographic Specialties Inc.)
- o-Terphenyl (Chromatographic Specialties Inc.).

3.4. Setup Materials

A search in the literature revealed that according to the newer references, for accurate measurements of hydrocarbons, particularly in the environmental samples, regular polymeric containers must be avoided. The conventional plastic equipment such as polyethylene, polyethylene, silicon and polyvinyl chloride (PVC) containers, centrifugal tubes and syringes show a high adsorption affinity to the hydrocarbons or leach trace residues, causing significant errors. Glass, stainless steel, aluminum and different types of Teflon (PTFE, FEP, PVDF, and PFA) are recommended for measurement of organic contaminants. Therefore, in the present study, all of the applied containers, tubes, vials, syringes etc. were made out of glass (Environment Canada, 2013; State Government of Victoria (Australia) Environmental Protection Agency, 2009; State of Ohio Environmental Protection Agency, 2006).

3.5. Analytical Methods

3.5.1. Sediment Water Content

Method ASTM D2216-10 (Standard Test Methods for Laboratory Determination of Water (Moisture) Content of Soil and Rock by Mass, 2010) was applied to measure the content of water in the sediment. Briefly, the difference between the weights of 5-gram samples was measured

before and after retaining in an oven with 105ºC for 18 hours, as shown in Equation 3.1. The average data of 5 measurements was used in further calculations.

$$W = \frac{W_{w-}W_{\mathrm{d}}}{W_w} \times 100 \qquad \text{Eq. 3.1}$$

where

W = water content (%)

W_w = weight of wet sample (g)

W_d = weight of dried sample (g)

3.5.2. Loss on Ignition (LOI)

Loss on ignition can be considered as an indicator for the total content of total organic carbon (TOC) in the environmental samples (Schumacher, 2002; Wright et al., 2008). To measure the loss on ignition, four 5-gram sediment samples which already had been dried at 105 ºC and the water content were known, were placed in an electrical furnace at 550 ºC for 4 hours. The difference between the weight before and after placing in the furnace was calculated, as shown in Equation 3.2. The average data was used in further calculations.

$$LOI = \frac{W_{f-}W_{\mathrm{d}}}{W_d} \times 100 \qquad \text{Eq. 3.2}$$

where

LOI = loss on ignition (%)

W_d = weight of dried sample (g) at 105ºC

W_f = weight of sample exposed to 550ºC (g)

3.5.3. Extraction of Pore Water

In the natural environment, when a pollutant already adsorbed into the solid phase is exposed to a liquid phase (e.g. water) an equilibrium is formed between the solid and liquid phases. To be able

to separately measure the concentrations of the hydrocarbon pollution distributed in the sediment and water, pore water needs to be separated from the solid part in the sediment. In the laboratory, pore water can be extracted by several different methods such as mechanical pressure and centrifugal force (Adams et al., 2001; Carr & Chapmam, 1995; USACE & SFWMD, 2009). For this purpose, in this study, a special centrifuge tube was designed and built. A stand and a metallic screen in the centrifuge tube allowed the water to escape from the solid and collect at the bottom of the tube. The internal layer of the tube was made from thin aluminum to minimize the adsorption of hydrocarbons on the walls. Sediment samples were centrifuged at 15000g at 5^{o}C for 35 minutes in a Thermo Scientific Heraeus Multifuge 3SR+ centrifuge. The water was collected and transferred to a 2.5 ml vial. The volume, weight, concentration of total petroleum hydrocarbon (TPH) and other parameters in the pore water were measured. Also, after separation of pore water, weight, water content, TPH content, and other parameters were determined in the sediment samples. Five samples were centrifuged, and the average data was used in further calculations.

3.5.4. Total Petroleum Hydrocarbon (TPH)

In this study the concentrations of TPH in sediment, pore water and processed water were measured by applying the C10-C50 analysis protocol established by the government of Quebec (MA. 400 – HYD. 1.1; Détermination des hydrocarbures pétroliers (C10 à C50): dosage par chromatographie en phase gazeuse couplée à un détecteur à ionisation de flame, 2013) (2013). This protocol was selected for its accuracy and safety. In brief, sediment samples were dried with 3.5 g magnesium sulfate and extracted by hexane in an ultrasonic bath for 15 minutes. By applying a different solvent to sediment ratios, it was found that the best GC peaks appear by adding 7 ml of hexane to the solid mixture. Then, the extracted hexane was purified by silica gel and injected to gas chromatography instrument. As well, 300 ml water was extracted at least two times by 20 ml of hexane in a separatory funnel. Then, hexane was dried with sodium sulfate, cleaned with silica gel and injected into the GC. If the concentration of the pollutant was lower than the lowest detection limit of GC, the extracted solvent was concentrated. The samples with fine particles were filtered with a 0.45 μm PTFE syringe filter placed on the tip of glass syringes to avoid damaging the capillary column in the GC.

A gas chromatograph coupled with a flame ionization detector (FID) (model Varian CP-3800) was used to measure the total petroleum hydrocarbon content in solid environmental samples and water. A capillary DB-5 column (Agilent Technologies) was used in the GC. By changing different parameters such as column temperature ramp, injector temperature, detector temperature, flow rate, split ratio, injection volume, detector voltage, amplification ratio, more than 100 situations were tried to find the optimum detection method on the GC (Table 3.2). The TPH measurements were duplicated or triplicated for solid and liquid samples.

3.5.5. Particle Size Analysis

A vigorous agitation involves an attrition process and reduction of the solid particle size. To investigate the effect and extent of size reduction, particle size analysis was performed for sediment particles before and after the desorption-sorption experiments. A Laser Diffraction Particle Size Analyzer (model Horiba LA-95V2) was used to determine the distribution of particle size of sediment before and after the desorption-sorption process over 10 to 3000 μm. The samples were collected in 50 ml Erlenmeyer flasks from the sediment-in-water slurry in the sorption-desorption process setup with the concentration of 10 g/l. The flasks were agitated by

Table 3.2. GC Conditions for measurement of TPH in sediment and water

Parameter	Value
Injector temperature	300°C
Detector temperature	300°C
Column temperature program	Initial temperature: 50°C; Hold for 6 min; Increase the temperature to 300 °C by a rate of 30 °C/min; Hold on 300°C for 15 min
Column flow rate	2 ml/min; constant
Injection size	5 μl
Split ratio	1:1

hand and 5 ml of the slurries were poured into the feeding funnel of the instrument by pipette. The distribution of particle size represents the content of colloid, clay, silt, and sand in the sediment. The measurements were performed in triplicate.

3.5.6. Fluorescence Microscopy

Fluorescence microscopy observation was performed for sediment particles and aerogel granules to investigate the visual difference between before and after the desorption-sorption process. An Omax Epi-fluorescence was used to perform the microscopy imaging. The wet sediment samples and aerogel granules were placed on a glass slide and observed under the fluorescence light. Aerogel granules were ground and flattened between two glass slides before placing in the microscope.

3.5.7. Electron Microscopy

Scanning electron microscopy (SEM) was applied to investigate the surface of sediment particles and aerogel granules before and after the desorption-sorption process. SEM imaging was done by a Hitachi S-3400N Scanning Electron Microscope. Sediment samples were dried in the air for 24 hours. Aerogel granules were kept 48 hours in the room temperature until the small droplets of water trapped between the granules evaporated. Sediment particles and aerogel granules were fixed on a carbon tape and covered by gold powder to increase the image contrast.

3.5.8. Bulk Density of Aerogel

The bulk density of the aerogel was measured by weighing 100 ml of aerogel inside a graduated cylinder placed on a lab balance and dividing the weight (g) by the volume (ml).

3.5.9. Adsorbent Contact Angle

As an indicator of hydrophobicity, the contact angle of aerogel was measured. Because of the granular shape of aerogel, the existing instrument for measuring the contact angle could not be applied properly. Therefore, a device including a tilted mirror was built and used with a Wild

Heerbrugg stereo-microscope. The contact angle was measured by placing a droplet of water (10 µl) on the surface of aerogel and taking images under the microscope in 120x magnification. Tens of trials were performed and the best images were selected. The angle was measured by a screen protractor on the electronic images.

3.5.10. Crude Oil Retention Capacity of Adsorbents

A modification of the standard method ASTM F726 (Standard Test Method for Sorbent Performance of Adsorbents) was applied (ASTM F726-99, 1999). A mechanism was designed and built to measure the uptake of crude oil by adsorbents (aerogel and granulated activated carbon) (Figure 3.5). A screen basket was made and about 0.1 to 0.5 g of aerogel and granulated activated carbon were placed inside the basket. The basket was hung from a stand and placed above a Petri dish touching the surface of liquid hydrocarbon, while the Petri dish was seated on a microbalance. The decrease in the weight of crude oil was registered in the 10-second time intervals. To consider the effect of evaporation, the tests were repeated in the same time period without contacting the adsorbent. The measurements were performed in duplicate.

3.5.11. Uptake of Hydrocarbon from Aqueous Phase, Adsorption Isotherms & Kinetics

The sediment-water slurries were agitated vigorously in an enclosed stainless-steel jar in 15900 rpm for 45 minutes and sediments were separated from the supernatant by centrifugation in aluminum tubes at 3700 rpm for 30 min before the adsorption tests. The uptake of hydrocarbon from water was measured by adding pre-weighed amounts of adsorbents (1 g for aerogel and 2 g for granulated activated carbon) into the mixtures of water and sediment-extracted hydrocarbons in the shaken glass bottles. The isotherm equations were calculated by addition of 0.1 to 1 g for aerogel and 1 to 4 g for granulated activated carbon to the water-hydrocarbon mixtures. The decrease in the TPH content of water was measured by GC at pre-specified time intervals. The experiments were repeated without adsorbent to consider the influence of parameters such as adsorption on the glassware or volatilization. Collected data was used for the determination of kinetic equations as well. The tests were duplicated to ensure the quality of the data.

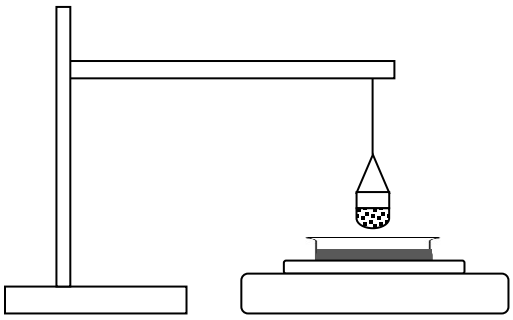


Figure 3.5. Schematic of the device for measurement of uptake of hydrocarbon pure phase by the adsorbent

3.5.12. Microscopic Imaging of Aerogel Particles

A Wild Heerbrugg stereo-microscope was used to take images of aerogel granules and observe the difference in the appearance before and after the adsorption from the pure hydrocarbon phase. As the diameter of the final image in the eyepiece was very small (about 4 mm), the best photographic results were achieved by placing a cell phone camera (having a very small lens) on the eyepiece of the microscope. The magnitude of x20 gave a clear image of granules.

3.5.13. Fourier Transform Infrared Spectroscopy (FTIR)

In the previous studies, Fourier transform infrared spectroscopy (FTIR) has been used to study chemical bonding and the network structure in aerogel (Parvathy Rao et al., 2007; Shewale et al., 2008). Zhang et al. (2015) applied FTIR spectroscopy to investigate the change in chemical bindings between Si, O, C and H before and after adsorption of hydrocarbons.

Fourier transform infrared spectroscopy was applied to investigate the type of bonding between constructing atoms and functional groups in aerogels. FTIR analysis was performed by a Thermo Scientific, 4700 FTIR spectrometer. Granules of fresh and processed aerogel were placed on a small flat diamond on the top of the instrument and were pressed to a flat layer by tightening a screw.

3.5.14. Thermogravimetric Analysis (TGA)

To investigate the effect of high temperatures on the network stability and change in chemical composition of aerogels during thermal regeneration, thermogravimetric analysis (TGA) was performed. The analysis was done by a TA Instruments TGA Q500 analyzer. The mass of aerogel granules was automatically recorded over time while the temperature increased from 35 to 900^{o}C during a 900-minute period.

3.5.15. Reuse of Aerogels

In the present study, thermal treatment and solvent extraction were investigated for the regeneration of the aerogels.

Regeneration by solvent: 15 ml of 5 different solvents including hexane, benzene, chloromethane, dichloromethane, and acetone were added to 0.25g of used aerogels vials and shaken for 15 minutes. Then, two phases were separated, and aerogel granules were kept under a fume hood for overnight to dry in the ambient temperature.

Regeneration by heat: based on gas chromatography data, petroleum hydrocarbon contaminants in sediments were in the range of C10 to C36. The highest boiling temperature for this range is possibly 265^{o}C for C36 (hexatriacontane). Therefore, three temperatures were selected for thermal regeneration of aerogels: 200, 250 and 300^{o}C. These temperatures were far below 400^{o}C where the aerogel granules significantly lost their weight due to thermal decomposition. At the same time, the temperatures were high enough to evaporate the hydrocarbon contaminants from the aerogel granules.

To study the effect of various regeneration temperatures on the structure of hydrophobic silica aerogels, Fourier transform infrared spectroscopy (FTIR) was performed. To find out the proper time length for regeneration, fresh aerogel granules, granules submerged under the water and granules used in the desorption-sorption process were placed inside an oven and the reduction in weight was recorded until there was no change in the weight up to 6 hours. All experiments were performed in duplicate. To investigate the number of the cycles that aerogel can be reused, the granules were repeatedly contacted with agitated sediments-in-water slurry and exposed to the heat inside an oven. The experiments were continued up to 10 cycles.

3.5.16. Mixer Rotation Speed

The rotation speed of the impeller in the mixer was measured using a stroboscopic laser tachometer rotation speed meter (model DT 2234C+). A small piece of shiny sticker (1x1 cm) was attached to a blade of agitator and the sensor of the tachometer was pointed perpendicular to the sticker. The number displayed on the tachometer was recorded in rpm. The measurements were repeated 10 times and the average value was calculated as the rotation speed.

3.5.17. Flow Rate, Gas Hold up and Hydraulic Retention Time (HRT)

The flow rate of slurry could be adjusted by two flow meters (low range and high range) and a pump controller on the control panel. The experiments were conducted at a flow rate of 4.5 l/min. After a series of experiments, it was found that this flow rate was the minimum flow rate in which the pattern of adsorption column stayed as a packed bed and not an inverse fluidized bed. In other words, at this downward flow rate particles of aerogel were not ascending to the surface of the water due to upward buoyancy forces. As well, the drag force of the flow of slurry was not high to contract the bed and compress the aerogel particles, which might result in a decrease in both bed height and particle porosity leading an increased pressure drop.

The working volume in the agitator was calculated by measuring the dimensions of the parabolic profile (h_0, H, and R) of the spinning water-air mixture according to Figure 3.6 and Equation 3.3.

$$H - h_0 = \frac{\omega^2 R^2}{2g} \qquad \text{Eq. 3.3}$$

where

H = Maximum height of the liquid (cm)

h_o = Minimum height of the liquid (cm)

ω = Rotational speed (1/s)

R = Radius of rotation

G = Gravity acceleration (9.8 m/s^2)

HRT was measured by applying Equation 3.4

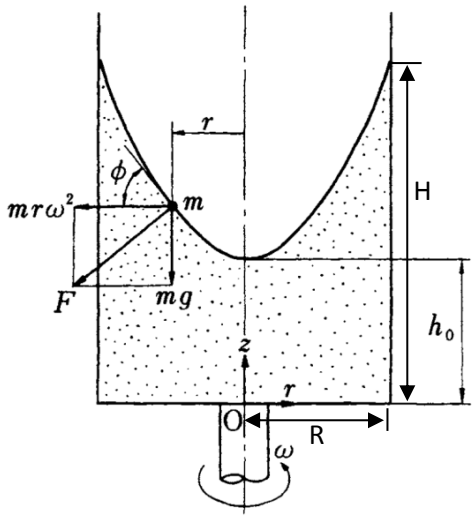


Figure 3.6. Parabolic profile of the liquid surface during the rotational movement in the mixer

$$HRT = \frac{V}{F} \qquad \text{Eq. 3.4}$$

where

HRT = Hydraulic retention time (sec)

V = Working liquid volume (cm^3)

F = Flow rate (cm^3/s)

The gas hold up (H) was calculated by subtracting the volume of the liquid from the volume of the liquid-gas mixture using Equation 3.5.

$$H = \frac{V_t - V_l}{V_t} \qquad \text{Eq. 3.5}$$

where

V_t = Total volume of the gas-liquid mixture

V_l = Volume of the liquid in gas-liquid mixture

3.5.18. pH, Dissolved Oxygen (DO) and Electrical Conductivity (EC)

During the tests, pH was measured by a Eutech Instruments pHTestr 30. Dissolved oxygen (DO) was measured using a portable dissolved oxygen meter Oakton 300 series. Electrical conductivity (EC) was measured by an Oakton 11 series conductivity meter. For measurements, slurry samples were collected from the sorption-desorption setup by 100 ml beakers and the data was read by placing the probe in the beaker. The measurements were in duplicate.

3.5.19. Effect of pH

In the desorption-sorption experiments as well as aerogel adsorption tests the effect of various pH was investigated by adjusting to acidic (pH 5) or basic (pH 9) conditions by addition of 0.01N HCl or 0.01N NaOH. Duplicate measurements were performed to assure the quality of data.

3.5.20. Effect of Solid Load

The effect of the solid load was studied by processing the sediment under different sediment to water weight/volume ratios (5, 10 and 15 g/l) in the desorption-sorption test setup. The measurements were performed in duplicate.

3.5.21. Effect of Mixer Speed

The effect of mixing intensity was studied by processing the sediment in five different mixing speeds: 2300, 6800, 10700, 15900 and 22100 rpm. The measurements were conducted in duplicate.

3.5.22. Effect of Retention Time (Flow Rate)

The flow rate of sediment slurry in the desorption-sorption experiments was 4.5 l/m. This flow rate was the minimum flow rate that the pattern of adsorption column stayed as a packed bed and not an inverse fluidized bed. To investigate the effect of retention time, the experiments were performed at a flow rate of 2 l/m. This flow rate was the minimum flow rate that the pump could work without a large head loss to interrupt the flow because of the pressure drop. The hydraulic retention time in the agitator for these flow rates were 11.5 and 26 seconds, respectively.

3.5.23. Effect of Salinity

To investigate the effect of salinity on the performance of the process, the desorption-sorption tests were performed in 3.5% aqueous solutions of salt (sodium chloride) to simulate sea water. The tests were in duplicate.

3.5.24. Effect of Temperature

The desorption-sorption experiments were conducted at laboratory ambient conditions while the temperature was in the range of 21-23 ^{o}C. To investigate the performance of the desorption-sorption process in different climates, the effect of temperature on the process was studied. Due to the large size of the desorption-sorption setup, it was impossible to move the setup to an outdoor environment, place it in an incubator or fridge, or insulate and cover all the parts by a thermal jacket. Therefore, the effect of temperature was investigated in separate batch desorption and sorption experiments at lab temperature and inside an incubator. To simulate the cold and warm climate, the temperature of the incubator was adjusted to 10 and 35^{o}C, respectively.

In the effect of temperature on desorption experiments, a slurry of 10 g/l of sediment in tap water was vigorously agitated in a stainless-steel mixer for 180 minutes. The time intervals were adjusted for 20 seconds ON and 60 seconds OFF applying a cyclic timer. The experiments were performed at 10, 22 and 35^{o}C. For studying the effect of temperature on sorption experiments, aerogel granules were contacted with water contaminated with hydrocarbon (as described in section 3.5.11) at 10, 22 and 35^{o}C. The concentration of TPH in water was measured by gas chromatography.

3.5.25. Power Consumption

Required power (Pietranski, 2012) was calculated by applying Equation 3.6

$$P = N_p \times N^3 \times D^5 \times \rho \qquad \text{Eq. 3.6}$$

where

P = Delivered power (kW)

N_p = Power number

N = Impeller speed (rps)

D = Impeller diameter (m)

ρ = Density of liquid (kg/m^3)

The density of slurry was measured as 1003.13 kg/m^3. The viscosity of slurry was calculated equal to 0.000958 Pa.s according to Eq. 3.7 (Stefanescu, 2015). Therefore, the ungassed Reynolds Number (~400,000) and gassed Reynolds Number (~266,000) represented a turbulent flow (>>10,000). In this flow pattern, the power number (N_p) is constant and equal to 0.65 (Trambouze, 2000).

$$\mu_s = \mu_l \times [1 + 2.5 f_s + 10.05 f_s^2 + 0.00273 \times exp(16.6 f_s)] \quad \text{Eq. 3.7}$$

where

μ_s =Viscosity of slurry (cP)

μ_l = Viscosity of liquid (cP)

f_s = Solid fraction

3.6. Sediment Quality

Sediment quality before and after the desorption-sorption process was evaluated based on the criteria for the assessment of freshwater sediment quality published by Environment Canada and Ministère du Développement durable, de l'Environnement et des Parcs du Québec (2007). The sediment quality evaluation considered the content of hydrocarbons, heavy metals, phosphorus, and nitrogen. The measured values were compared with rare effect level (REL), threshold effect

level (TEL), occasional effect level (OEL), probable effect level (PEL) and frequent effect level (FEL).

3.6.1. Heavy Metals

While sediments are contaminated with heavy metals, a vigorous turbulence causes the extraction of heavy metals from the sediments and therefore, an increase in the heavy metal concentration in the water. The adsorption of heavy metals by silica aerogel may or may not supersede the desorption phenomena by a strong agitation. In order to investigate the amount of heavy metals in the sediments and water, the content of heavy metals was studied before and after the desorption-sorption process.

To study the effect of the desorption-sorption process on the fate of heavy metals an inductively coupled plasma mass spectrometry (ICP-MS) instrument (model: Agilent Technologies 7700) was used. Heavy metal concentrations were measured in the sediment samples, pore water, and process effluent water before and after a vigorous agitation (without using aerogels) and the desorption-sorption process. The modified EPA method 3050B (Acid Digestion of Sediments, Sludges, and Soils) was used to digest the sediment samples (USEPA, 1996a). Briefly, 10 ml of a mixture of 30ml:8ml of HCl 37% and HNO_3 70% were added to about 0.5 grams of sediment samples and kept in 95 ^oC for 4 hours in a DigiPREP Jr heater. The digested samples were diluted to 50 ml and then 10 times with a mixture of 5% HCl and 1% HNO_3. The diluted samples were centrifuged in 3700 rpm for 10 minutes and then passed through a 0.45µm filter before ICP-MS analysis. The water samples were diluted 2 times with a mixture of 5% HCl and 1% HNO_3 and filtered via a 0.45µm filter before ICP-MS analysis.

3.6.2. Phosphorus

Total phosphorus content in the sediments and water was measured to investigate the effect of the desorption-sorption process on the fate of phosphorus extracting from sediments into the water. The content of phosphorus in sediments before and after the desorption-sorption process was measured by an Inductively Coupled Plasma Mass Spectrometry (ICP-MS) instrument (model: Agilent Technologies 7700). Phosphorus was extracted by the HCl Method (Ruban et al., 1999).

According to this method, 0.2 grams of fresh and processed sediment samples were weighed in crucibles and calcinated at 450^{o}C for 3 hours. Then, the ash was transferred into centrifuge tubes and 20 mL of 3.5M HCl was added. The tubes were stirred on a shaker at 120 rpm for 16 hours. Tubes were centrifuged at 2000g for 15 minutes. The liquid was filtered through a 0.45 μm filter before analysis by ICP-MS instrument.

The concentration of phosphorus in pore water and process effluent water before and after the desorption-sorption process was measured by a Hach Phosphorous TNT 843 kit. This method is based on the reaction of phosphate ions and molybdate/antimony ions in an acidic solution to form an antimonyl phosphomolybdate complex. The complex was reduced by ascorbic acid to phosphomolybdenum blue and was measured by a 2800 Hach spectrophotometer.

3.6.3. Nitrogen

To investigate the effect of the desorption-sorption process on the fate of nitrogen, the concentration of total nitrogen (including total Kjeldahl nitrogen and NO_3-N + NO_2-N) in process water before and after processing the sediments was measured by a Hach TNT 880 kit. The method TNT 880 uses a DRB 200 Reactor for reflux heating and a DR 2800 Hach spectrophotometer. Briefly, bonded inorganic and organic nitrogen was oxidized to nitrate by digestion and was measured by spectrophotometry.

3.7. Chapter Overview

A desorption-sorption process setup was designed and built as the optimum design for conducting the experiments. The setup included a forced desorption (vigorously agitated) vessel, a gas-liquid separation chamber, an adsorption (aerogel) column, pump, two-range flow meters, and a control panel. The slurry of TPH-contaminated sediments in water was exposed to ON/OFF cycles of agitation for 3 hours. The effect of various parameters (temperature, pH, solid load, salinity, agitation speed and retention time) was studied. Particle size analysis was performed for the sediment. Density and contact angle of the aerogel were measured. The adsorption capacity of aerogel was measured, and adsorption isotherms and adsorption kinetics were calculated. Scanning

electron microscopy (SEM) was applied to observe the surface change. Power consumption at different agitation speeds was calculated. Dissolved oxygen and electrical conductivity of sediment-in-water slurries were measured. The fate of heavy metals, phosphorous and nitrogen were studied. Regeneration of aerogels by solvent and heat was investigated by Fourier Transform Infrared Spectroscopy (FTIR) method.

Chapter 4 – Results and Discussion

4.1. Sediment Characterization

4.1.1. Particle Size Distribution

The result for particle size distribution in unprocessed sediment is presented in Figure 4.1. The sediment was formed mostly from colloid (51%), clay (31%) and silt particles (13%) and the rest from sand (0.2%). According to the Unified Soil Classification System (USCS) the sediment was classified as clay (ASTM D2487-17, 2006). After processing the sediment in the desorption-sorption setup, the size distribution changed, and the fraction of finer particles increased. In other words, the average volume of sediment particles was reduced under the mechanical shear (Figure 4.2). Sediments mean size reduced from 3.7-5.7 μm for unprocessed sediment to 0.69-0.75 μm for processed sediments. Reduction of size means having a higher specific surface per weight. The higher specific surface results in more attrition by the water-particle shear stress as well as increasing probability of particle-particle impacts. By increasing the agitation speed, the portion of finer particles increased. Petavy et al. (2009) showed that the remediation process during mechanical remediation can be either by removing the contaminated outer layer of the particle or breaking the particle into smaller parts or a combination of both.

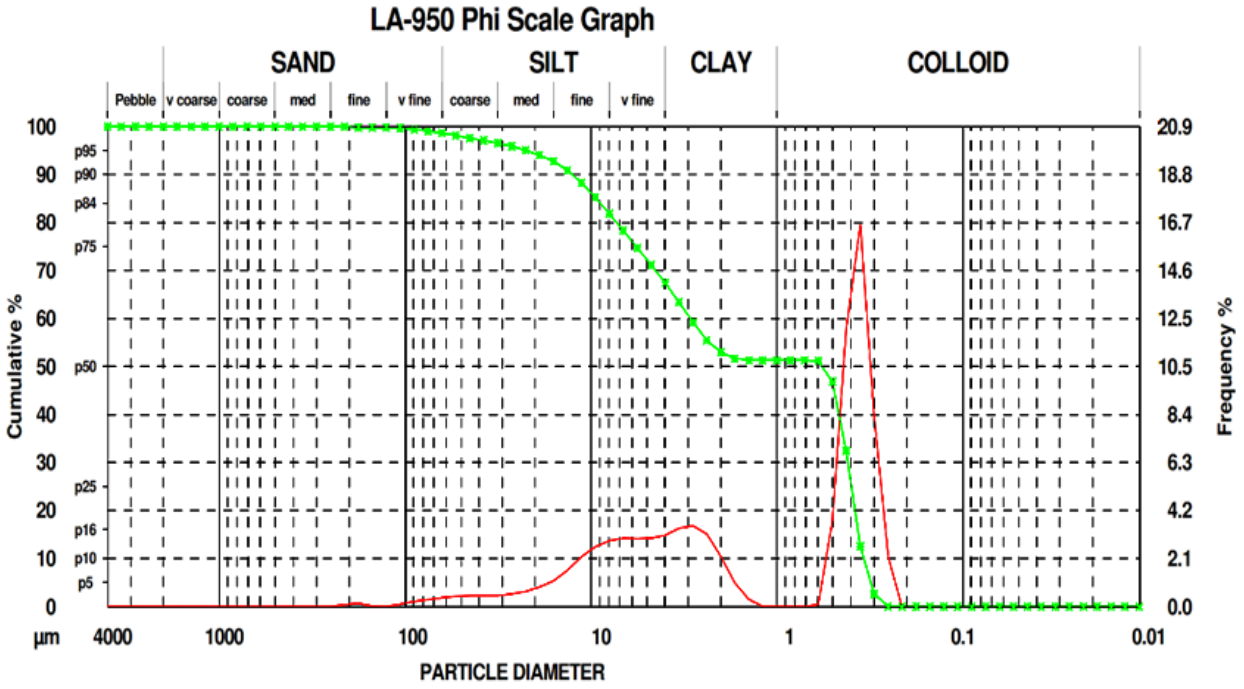


Figure 4.1. Distribution of particle size in the sediment before the process (µm) shown by the frequency (red line) and the cumulative frequency (green line).

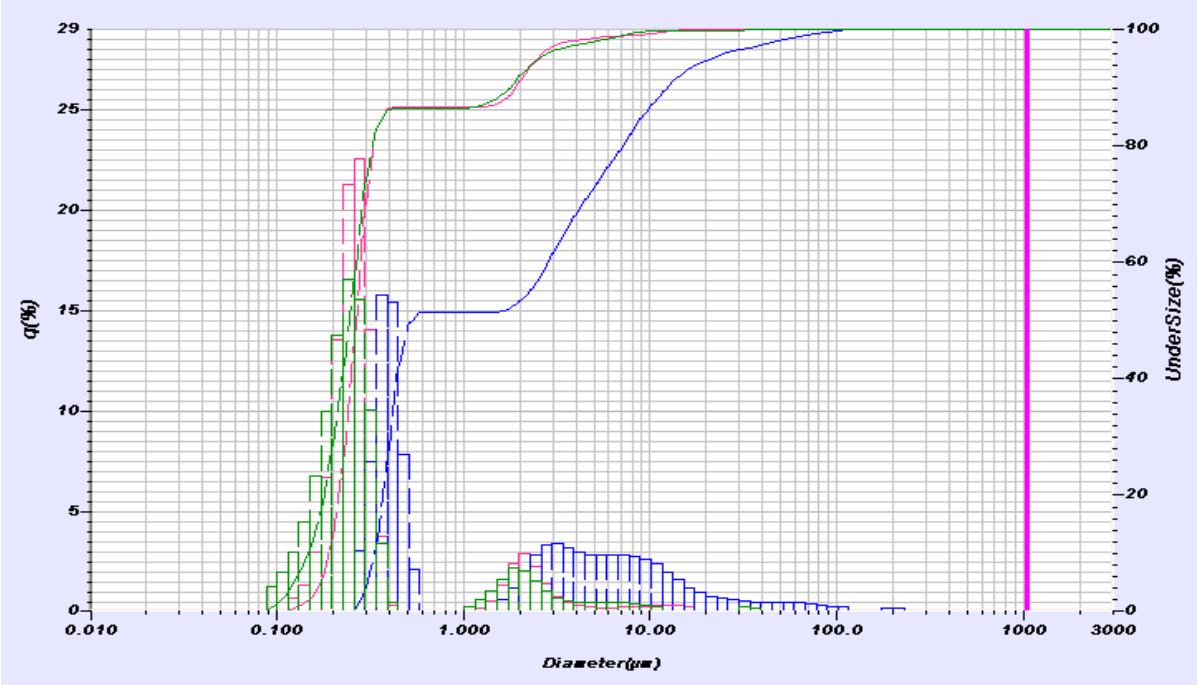


Figure 4.2. Change in the distribution of particle volume in sediment before (blue graph), after the process at15900 rpm (purple graph) and at 22100 rpm (green graph)

4.1.2. Water Content & Loss on Ignition (LOI) in Sediment

The water content was measured as 40.9 ± 0.8%. The water content was used in calculating the content of hydrocarbon on a dry basis. The loss on ignition (LOI) of homogenized sediment was 8.9 ± 0.4% indicating a high content of organic carbon which can lead to a more difficult remediation.

4.1.3. Hydrocarbon Contamination Analysis

The gas chromatograms showed that hydrocarbon contaminants form an unresolved complex mixture (UCM) in which the number of carbons fell in the range of C10 to C36 (Figure 4.3). Therefore, the hydrocarbon contamination could be indicated as total petroleum hydrocarbon (TPH) which is usually considered from C6 to C50 (CCME, 2008).

UCM chromatograms occur when a mixture of hydrocarbons is released into the environment and undergoes physical, chemical and microbial transformations such as weathering and biodegradation. UCM may consist of thousands of different hydrocarbon molecules (Kondla et al., 2016; Monza et al., 2015). The sediment samples used in this research had been under the influence of environmental factors for decades and represent a UCM chromatogram.

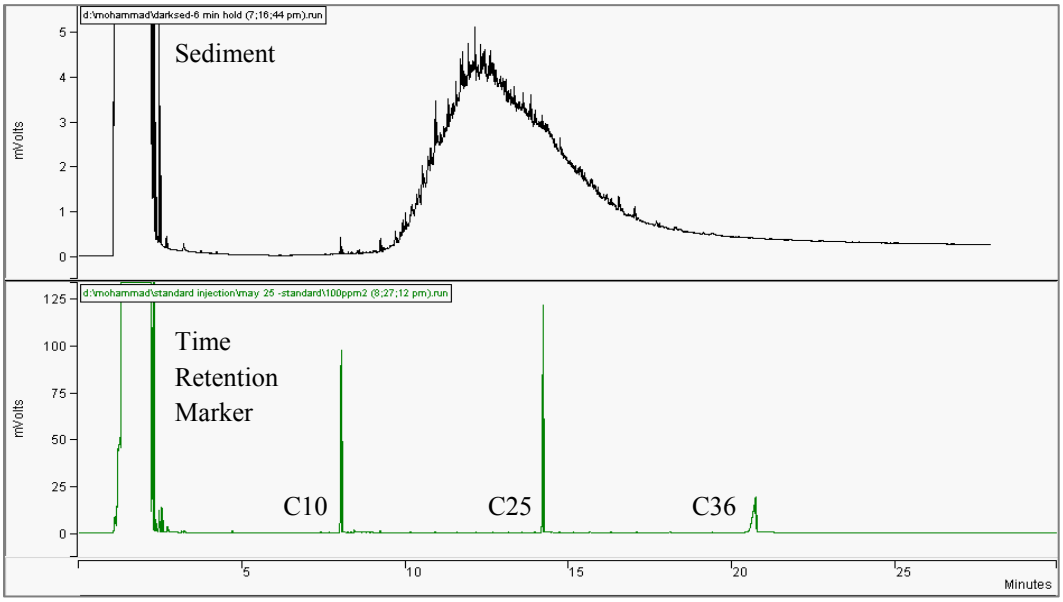


Figure 4.3. Identifying the range of hydrocarbon contamination in the sediment

4.1.4. TPH Content in Sediment and Pore Water

The concentration of contaminant hydrocarbons in a UCM is expressed cumulatively consisting the concentration of all existing hydrocarbons. In this research, the sediment sample contained 678.7 ± 21.0 mg/kg TPH in dry weight basis. According to the Canada federal and Nova Scotia regulations, the highest allowed concentration of TPH in the freshwater and marine sediments is 500 mg/kg in dry basis.

The sediment contamination with TPH occurred a long time ago. Therefore, there had been diffusion of hydrocarbon from sediment to the pore water and vice-versa. The concentration of TPH in water was 51.2 ± 3.7 mg/l showing a lower content of TPH, indicating a high affinity of the hydrocarbon by the sediment. Also, it indicated that the small fraction of TPH released into the water during the desorption-sorption process originated from pore water.

4.2. Desorption-Sorption Remediation Experiments

4.2.1. Sediment Processing in Desorption-Sorption Setup

The results of processing the sediment by the desorption-sorption process in 3 hours with the rpm of 15900 and flow rate of 4.5 l/min are presented in Figures 4.4 and 4.5. The final remediation of the hydrocarbon pollution in sediment was 29.5%. The solid fraction of the sediment was remediated by 25.6%. All TPH content of the pore water was extracted and adsorbed onto the aerogel. Also, the leaching of the hydrocarbon contaminant from the sediment was measured in the absence of agitation (for acceleration of desorption) and absence of aerogel (for adsorption of released TPH). Figure 4.5 indicates that in this case, the increase in the TPH content of process water was almost completely due to the release of TPH from pore water into the process water. To evaluate the effect of adsorbent by itself, the desorption-sorption tests were performed without placing the aerogel in the adsorption column. The results indicated the rerelease of TPH from both pore water and sediment. Furthermore, a series of experiments was conducted without applying vigorous agitation to observe the role of the aerogel itself for adsorption of TPH from the wet sediment. The results indicated the transfer of TPH was from mostly the pore water and adsorption on to the aerogel. By placing the sediment in water inside a static beaker the natural leaching of the TPH content from sediment was measured.

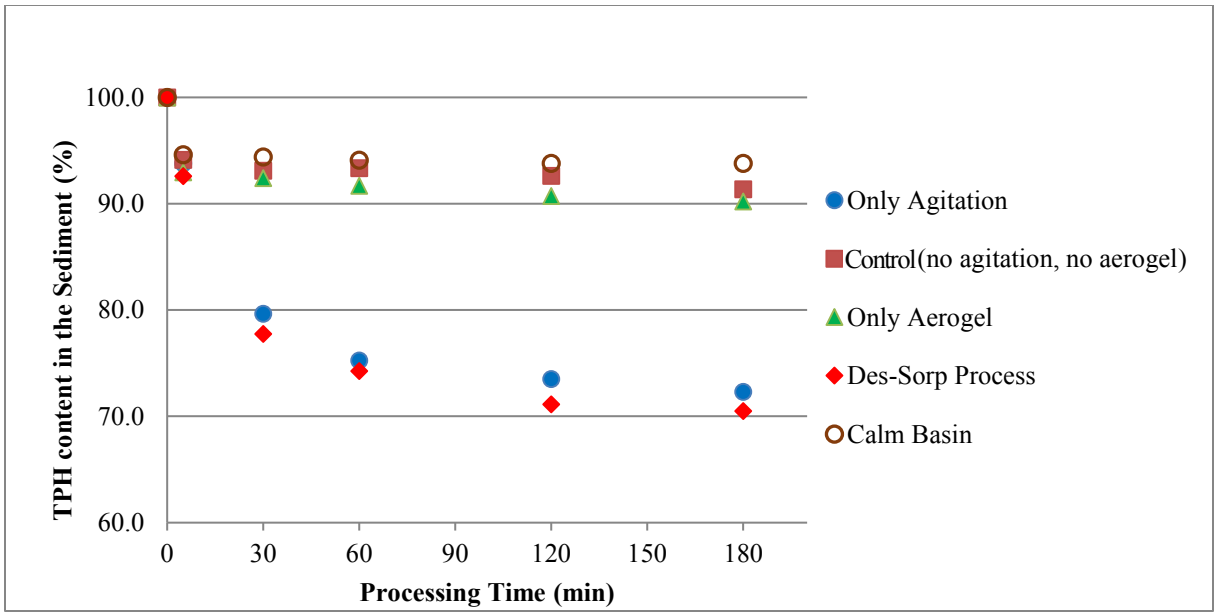


Figure 4.4. Comparison between the four series of 3-hour experiments: applying agitation and adsorption for remediation of sediment, only agitation, the presence of only adsorption, control (no agitation, no adsorption) and calm basin; the average values of duplicate measurements are presented on a wet basis (error margin ≤ 4%).

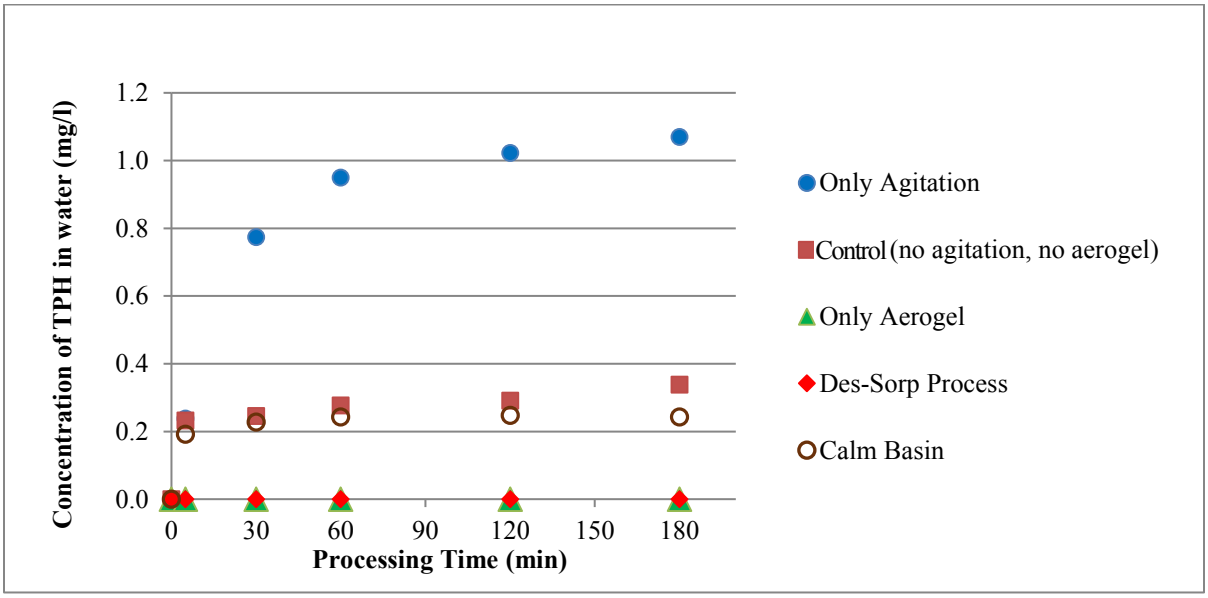


Figure 4.5. Comparison between the four series of 3-hour experiments: applying agitation and adsorption for remediation of sediment, only agitation, the presence of only adsorption, control (no agitation, no adsorption) and calm basin. The average values of duplicate measurements are presented for the concentration of TPH in the process (error margin ≤ 4%).

4.2.2. Fluorescence Microscopy

Fluorescence microscopy observation (x100) showed that the number of small droplets of hydrocarbons trapped in contaminated sediment particles was reduced after the desorption-sorption process in comparison with unprocessed sediments (Figure 4.6). Aerogel particles which have been used in the process showed a dimmed shine, as an indication of hydrocarbon sorption (not shown here).

4.2.3. Variation of pH, DO and EC in Desorption-Sorption Process

The variations in pH, dissolved oxygen (DO) and electrical conductivity (EC) are presented in Figures 4.7 through 4.9. While DO and EC did not follow a specific change after an initial increase, pH increased slightly during the process in the absence of agitation. Applying a vigorous agitation caused a more visible increase in pH. According to Sillanpää (2011), the micro-size cavitation and high temperature spots (formed due to applying power) produce anionic hydroxyl radicals (OH-) and increase pH. Also, the increase in pH could be due to the dissolution of anionic low-soluble salts in the water. EC and DO were relatively higher when agitation was applied.

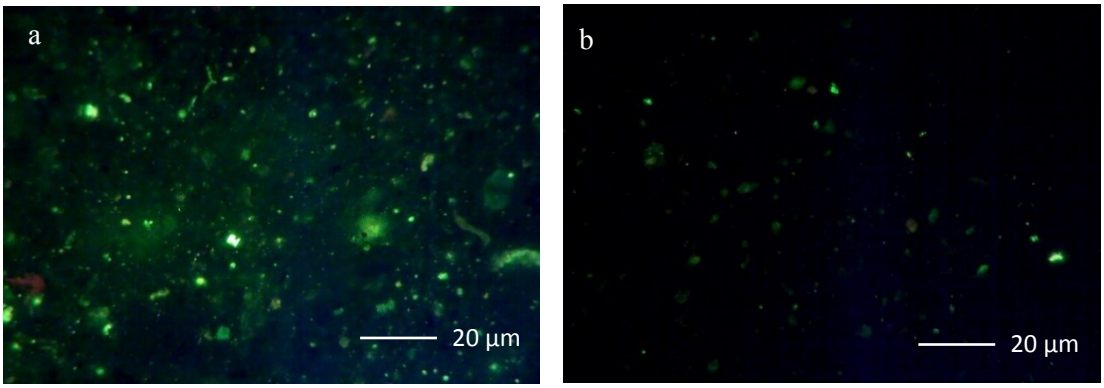


Figure 4.6. Representation of shiny spots of trapped hydrocarbon in sediments (a) before and (b) after desorption-sorption process under the fluorescence microscope (The white bar represents 20 µm.)

The increase in EC can be attributed to the release of conductive charged ions from the sediment into the water. The increase in DO was predictable, as the agitation increased the contact of water and air leading to a higher content of dissolved oxygen in the water.

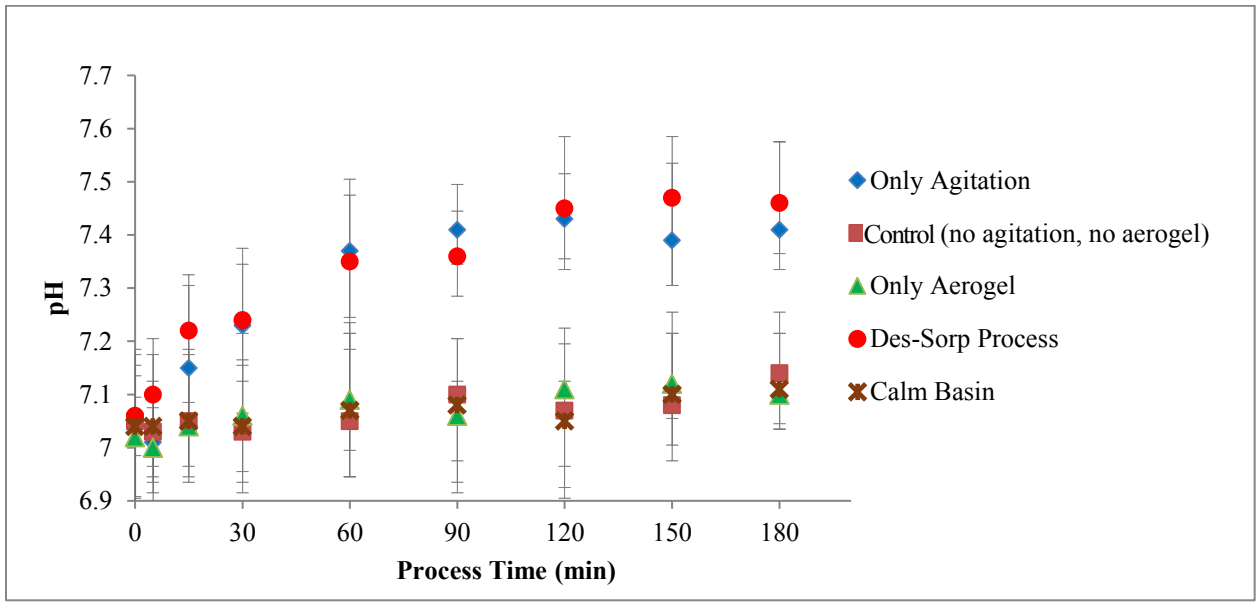


Figure 4.7. Variation of pH during the sediment desorption-sorption process

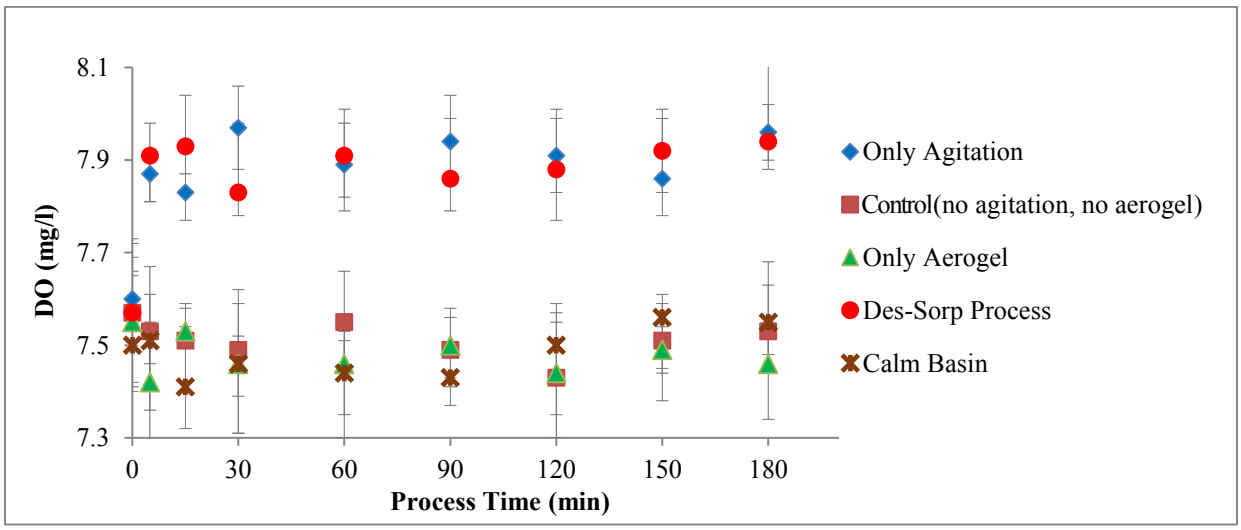


Figure 4.8. Variation of dissolved oxygen (DO) during the sediment desorption-sorption process

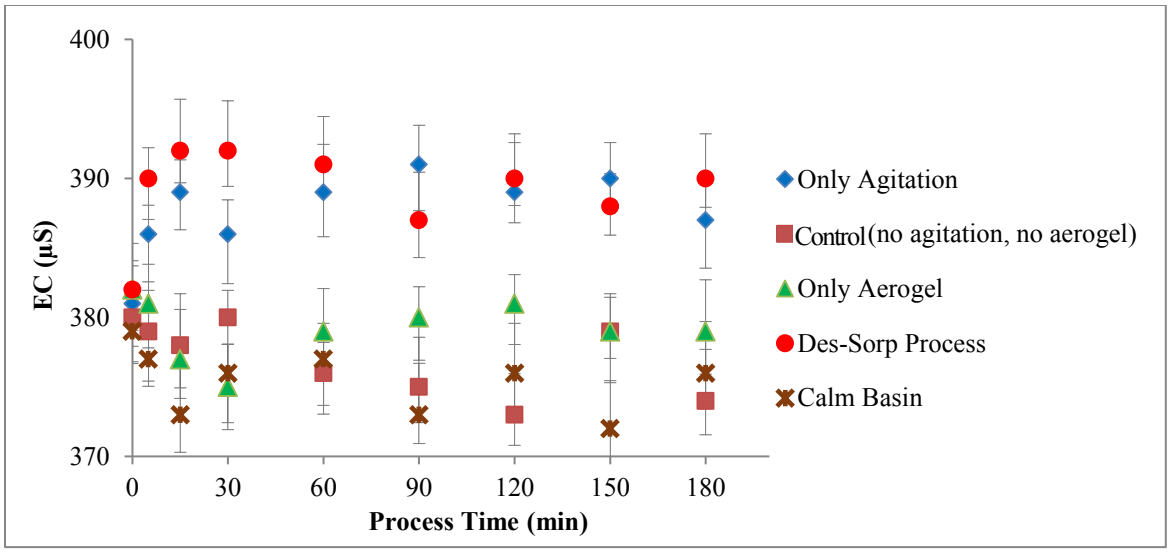


Figure 4.9. Variation of electrical conductivity (EC) during the sediment desorption-sorption process.

4.2.4. Effect of pH

The effect of pH on the content of TPH in sediment and water in different configurations of treatment is presented in Figures 4.10 and 4.11. The effect of pH was negligible with agitation. In this study, the pH was close to neutral. Therefore, there was not a significant change in the desorption of TPH from sediment by variations of pH, though, Moon et al. (2016) reported that increasing the concentration of HCl, HNO_3 and H_2SO_4 solutions (from pH 3 to pH 0.1) increased the removal of TPH from the soil. In another study, deasphalted crude oil did not show adhesion to outcrop rocks in the low-pH range (Buckley & Morrow, 1990). Also, according to Strassner (1968) emulsions of crude oil-water with pH<5 were highly stable; while at pH>10 they showed low stability or were highly unstable. Daaou and Bendedouch (2012) showed that an Algerian crude oil emulsion was relatively stable at moderately basic pH. In a series of experiments by Wang and Alvarado (2008) particle-stabilized emulsions of crude oil-in-water were studied by addition of kaolinite and kaofine. Both emulsions exhibited higher stability in acidic pH in comparison with neutral pH. They concluded that the difference in removal of oil from the soil and sediment can be attributed to the wettability of the surface and stability of the oil-in-water solution. The effect of pH on desorption was superseded by the vigorous turbulence in desorption-sorption process. The effect of pH on the adsorption capacity of aerogel is discussed in section 4.3.7.

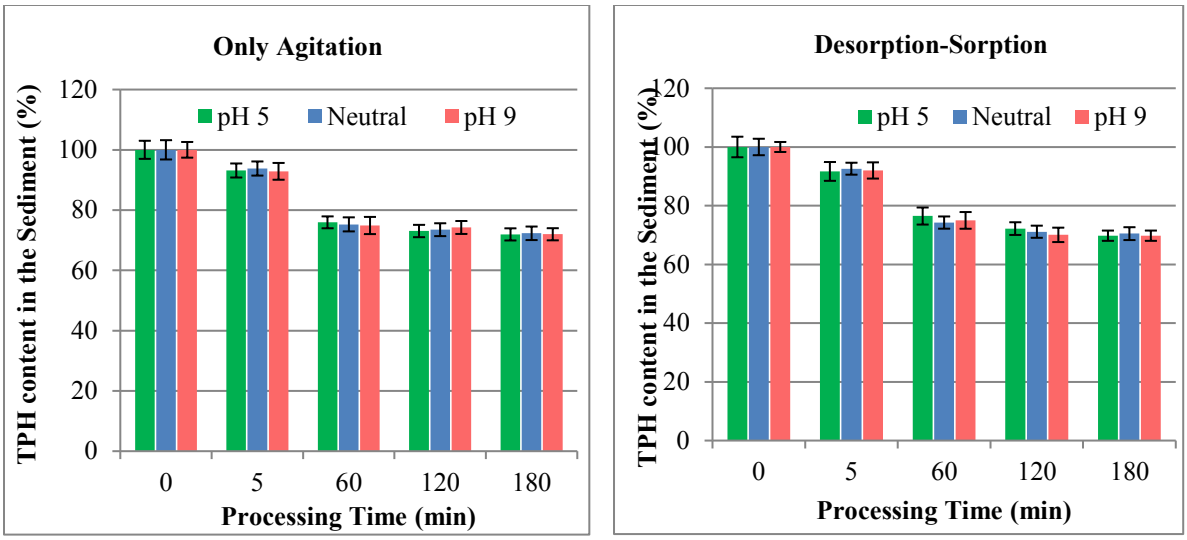


Figure 4.10. The effect of pH on the sediment remediation

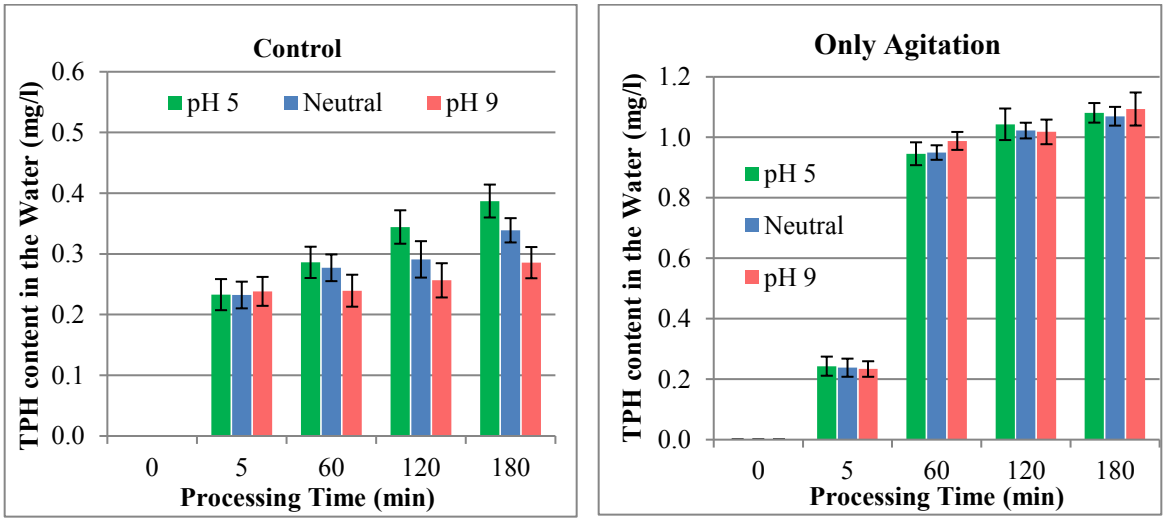


Figure 4.11. The effect of pH on the release of TPH into water

4.2.5. Effect of Solid Load

The effect of sediment loading on the content of TPH in sediment and water in various process configurations is shown in Figures 4.12 and 4.13. Solid load affected proportionally the release of TPH into the water but did not have any visible effect on the concentration of the contaminant in the sediment.

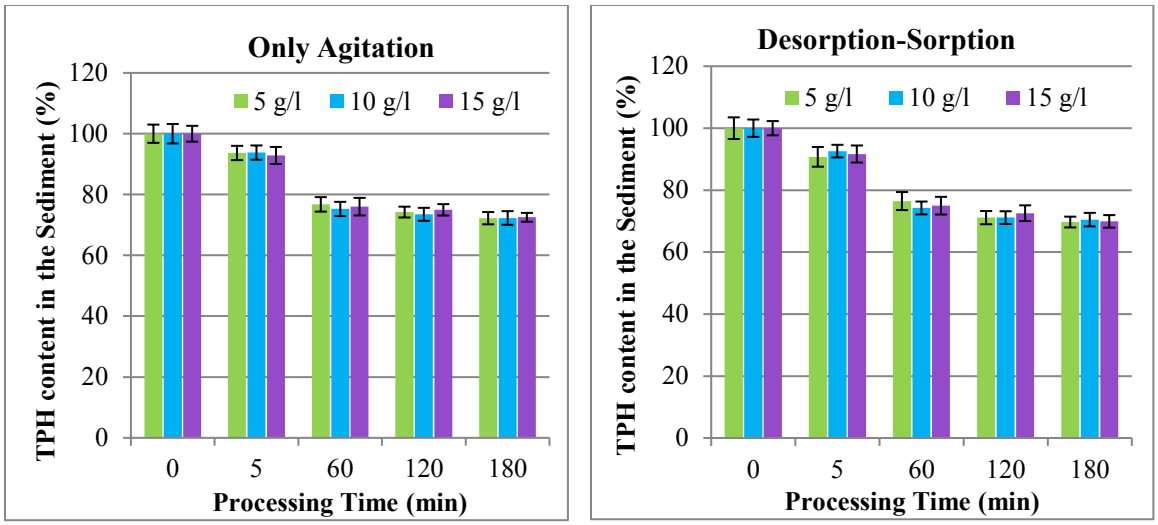


Figure 4.12. The effect of solid load on the sediment remediation in the desorption-sorption process

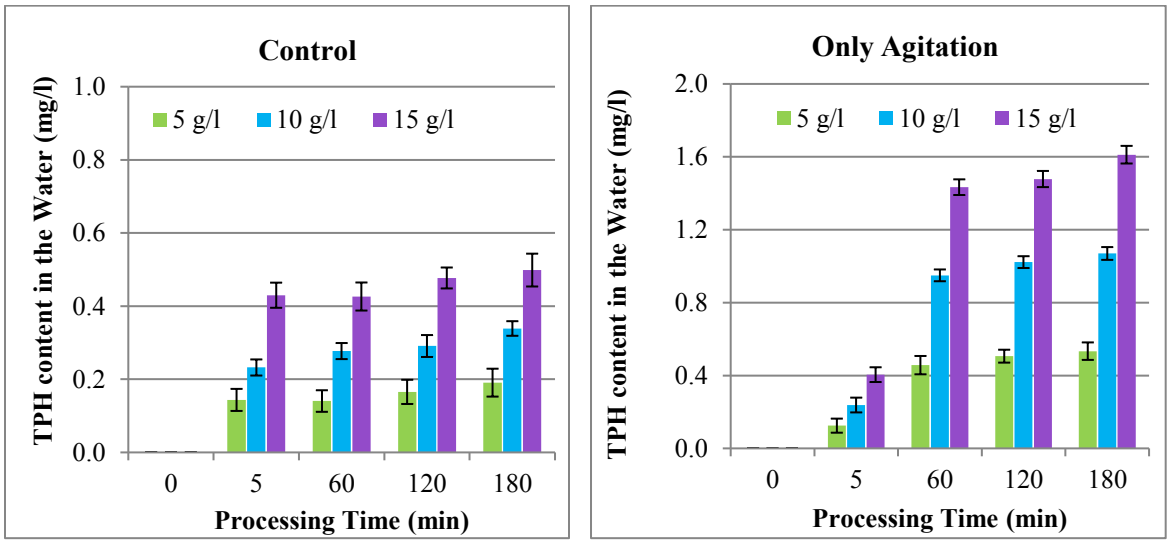


Figure 4.13. The effect of solid load on the release of TPH into the water when only agitation is applied

Previous research indicated that the critical impeller speed for the complete suspension of floating solid particles did not significantly change with solid load (Kuzmanić, 2008). On the other hand, Feng et al. (2001) used a jet reactor, ultrasound, and attrition washing to remediate a soil contaminated with diesel. They used high solid concentration ranges from 10% to 20% for the jet reactor, 20% to 70% for ultrasonic washing, and from 70% to 90% for attrition washing. The three methods did not follow the same pattern. By increasing the soil content, the efficiency of diesel

removal in the jet reactor washing reached a maximum and then decreased, whilst in ultrasound and attrition washing, the removal efficiency decreased to a minimum and then increased. They concluded that for diesel removal at lower solid concentrations, by increasing the solid/liquid ratio, the effect of interparticle scrubbing increases and becomes dominant over particle-water shear. In the current study, the concentration of solids was significantly lower when particle-to-particle scrubbing came into effect (5 to 15 g/l). Therefore, the particle-water shear governed the desorption process.

4.2.6. Effect of Impeller Rotation Speed

The effect of impeller rotation speed in agitation vessel on the content of TPH in sediment and water is shown in Figures 4.14 through 4.15. It is obvious that the release of TPH from the sediment was directly dependent on the speed of impeller or input mixing power in the agitation vessel.

Reduction of size is an important mechanism in remediation of sediment. According to Bayley & Biggs (2005b), a main part of remediation can be done by the detachment of fine particles from a soil cluster resulting in a higher exposure of contaminants to the turbulent surrounding. In another study by Bayley & Biggs (2006a), small particle sizes had a lower final contamination concentration after mechanical remediation by a jet pump.

At the higher speeds, the shear increases and causes the impact or attrition of particles resulting in a smaller size. Therefore, the exposure of TPH contamination to the water vortices increases. Also, the impact of vigorous agitation loosens the bonds between hydrocarbon contamination and sediment.

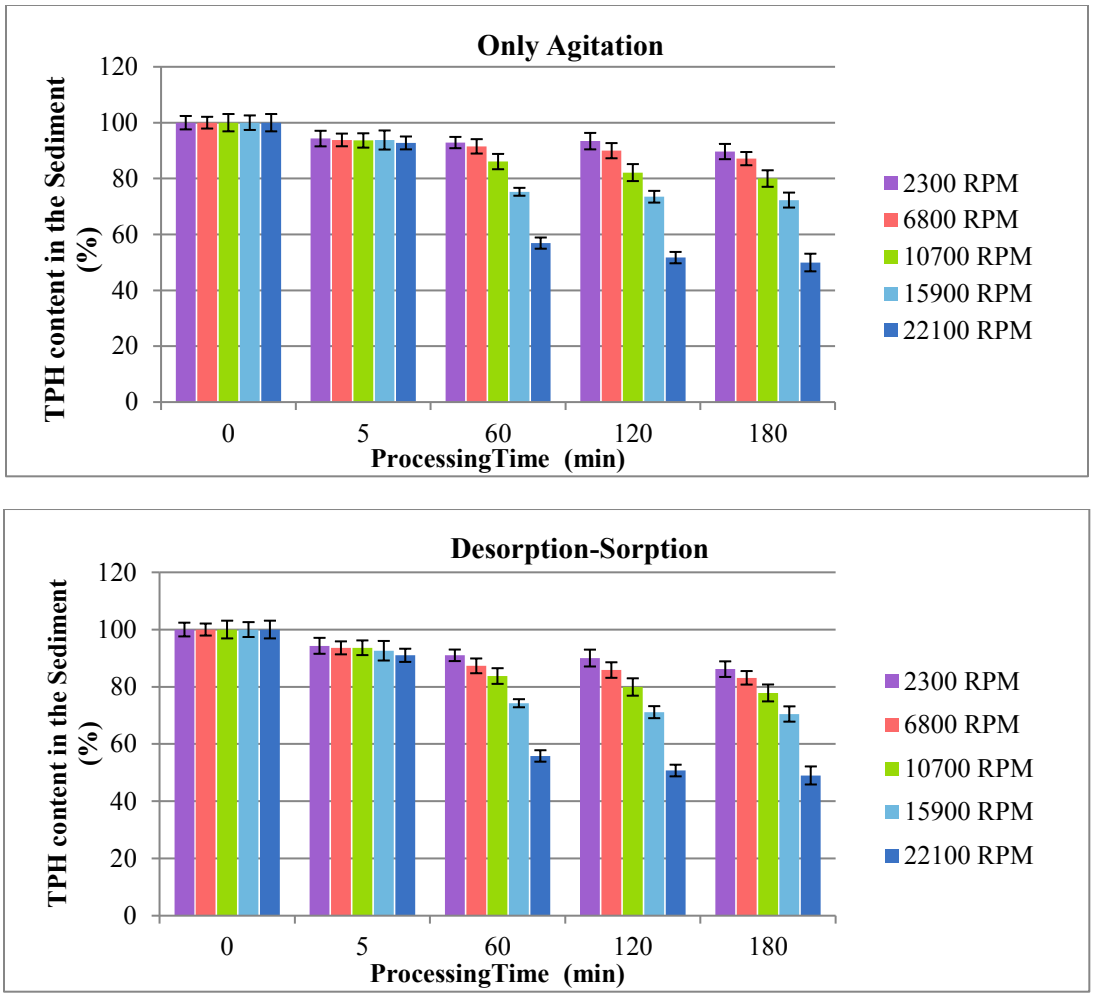


Figure 4.14. The effect of impeller rotation speed on the sediment

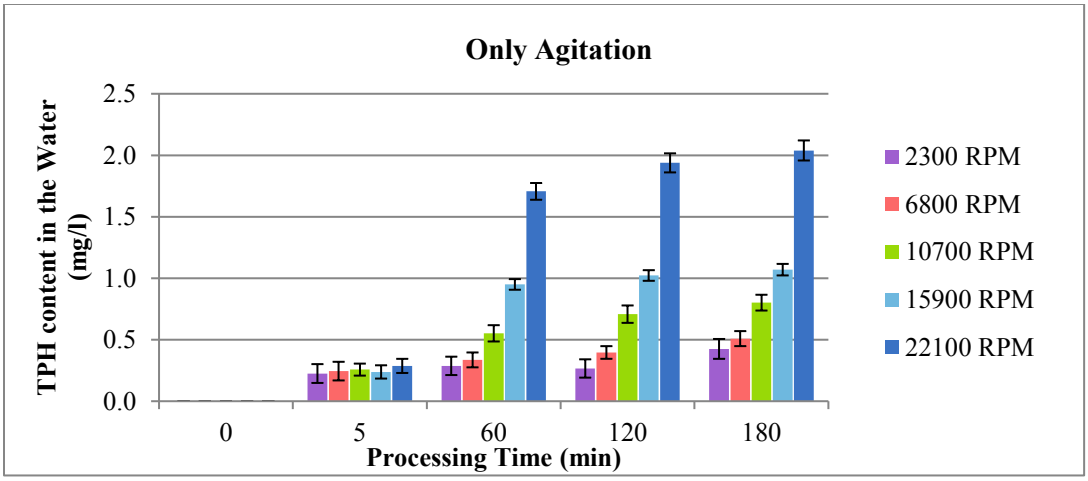


Figure 4.15. The effect of impeller rotation speed on the release of TPH into the water

4.2.7. Effect of Retention Time (Flow Rate)

The effect of retention time in the agitation chamber on the content of TPH in sediments and water is shown in Figure 4.16. Retention time did not show any significant effect on the concentration of contaminants in the sediment. The desorption-sorption process was a closed-loop system and the flow rate was high in comparison with the total volume of the system. Therefore, all the slurry circulated in the system several times every minute. By increasing the flow rate, the average retention time for every particle of sediment or a small control volume of water became shorter, but the number of passes through the agitation chamber increased, which negated the short residence time.

4.2.8. Effect of Salinity

The effect of salinity on the content of sorption-desorption is shown in Figure 4.17. The salinity did not represent a significant effect on the sorption-desorption process. In this study, freshwater sediments were used. According to Love et al. (2005), salinity did not have a significant effect on the adsorption capacity of hydrophobic silica aerogel. Salinity was favorable for aggregation of oil with sediment particles (Sun and Zheng, 2009), but it was not favorable for dissolution of hydrocarbons in water (Lamichhane et al., 2016). These two phenomena became negligible after TPH was detached from the sediments under the influence of a vigorous turbulence resulting in an insignificant effect on the desorption-sorption process.

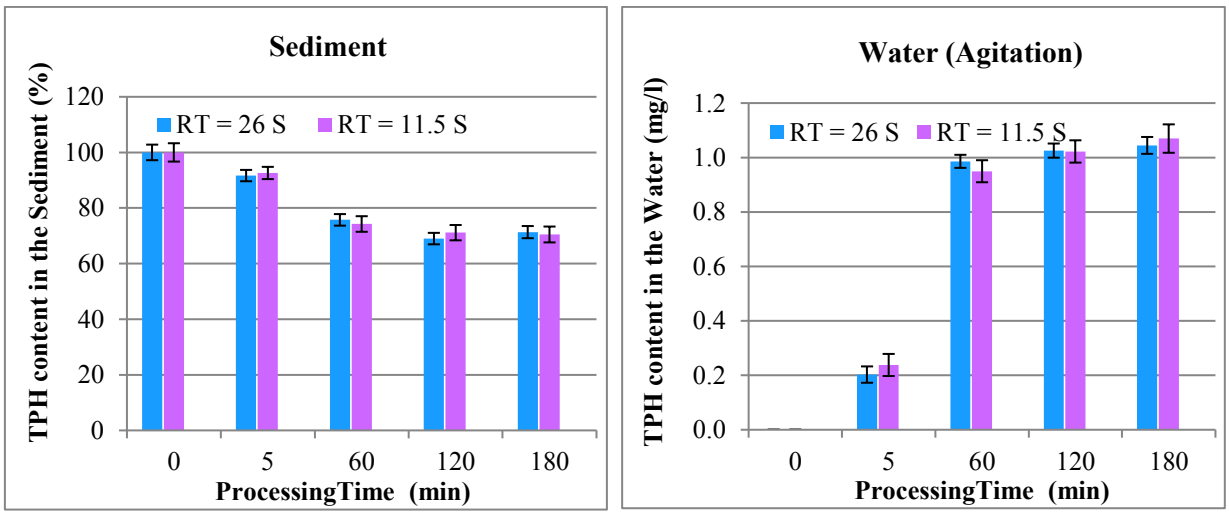


Figure 4.16. The effect of retention time on the TPH content in sediment and water

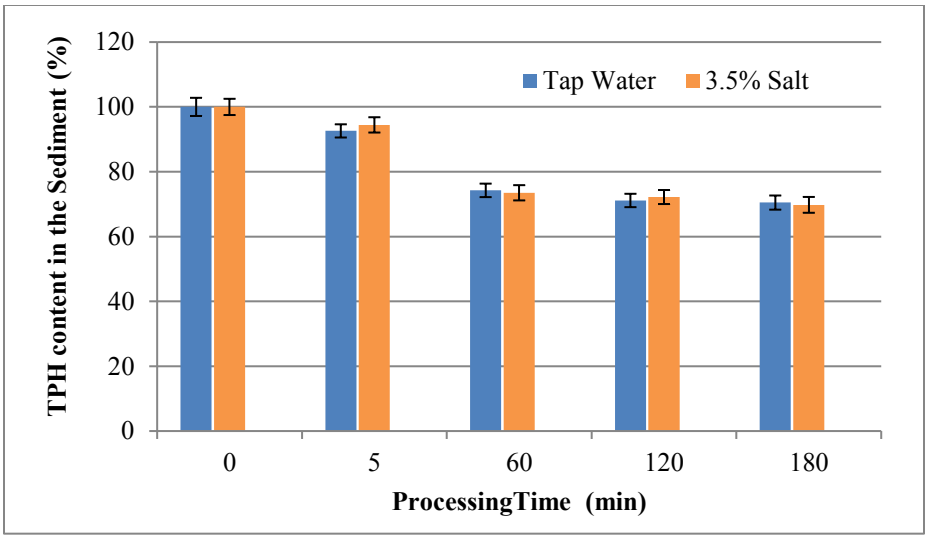


Figure 4.17. The effect of salinity on TPH content of sediment in desorption-sorption process

4.2.9. Effect of Temperature

The effect of warm and cold temperature on the desorption of TPH from sediments is shown in Figure 4.18. The effect of warm and cold temperature on the adsorption of TPH by aerogel granules is discussed in section 4.3.8. At a lower temperature (10°C) the desorption of petroleum hydrocarbons from sediments was less than the ambient temperature (22°C) and in the higher temperature (35°C) the desorption was higher.

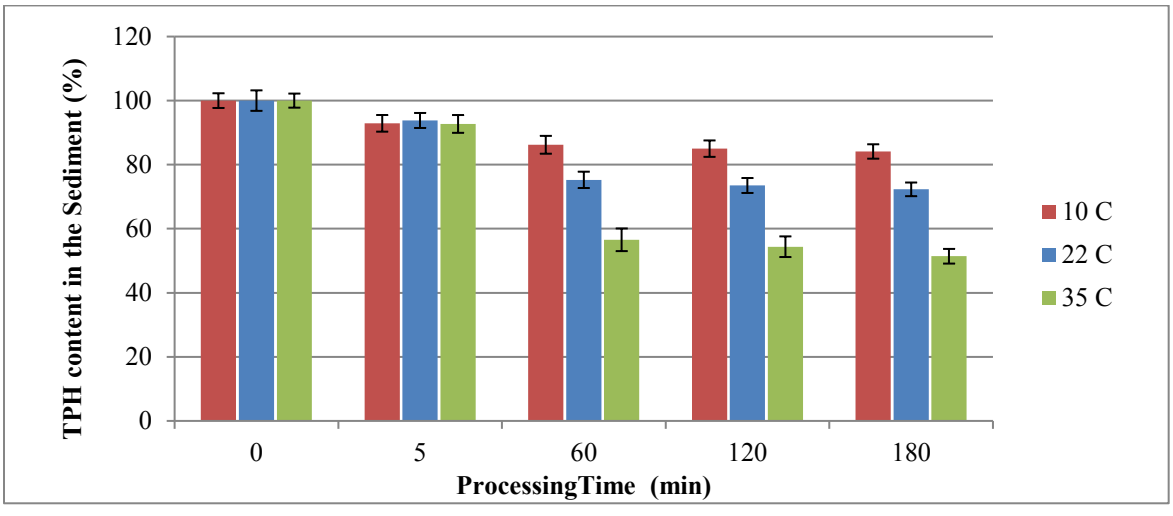


Figure 4.18. The effect of temperature on the desorption of TPH from sediment

Khelifa et al. (2002) studied the effect of temperature on the detachment of oil from oil-mineral aggregates in 0ºC and 20ºC. They reported that the content of oil droplets decreased rapidly by increasing temperature. They concluded that the number of oil droplets stabilized by mineral particles is reversely influenced by the effect of temperature on oil viscosity. Long et al. (2005) studied the effect of temperature on extraction of bitumen from oil sands. They reported that by increasing temperature, adhesion forces between clay and bitumen decreased until a critical temperature about 32-35°C. Above this range, the adhesion force diminished. Decreasing temperature led to the lower bitumen recovery from oil sand. According to Hiller et al. (2008), the sorption of PAH onto sediments decreased by increasing the temperature from 4°C to 27°C. They concluded that partitioning of PAH into the organic matter was the main mechanism. Podoll et al. (1989) reported that adsorption of naphthalene on soil is an exothermic phenomenon and decreased when the temperature increased from 15 to 50°C.

4.3. Adsorbent Characterization

4.3.1. Aerogel Bulk Density

The bulk density of the aerogel used in this study was measured and equal to 61.3 g/l. According to the aerogel's manufacturer (Cabot Inc.), the density of the aerogel particle was 120 – 180 g/l which was 5.5 to 8.3 times lighter than water. The difference can be attributed to variations in the batch formulation and the physiochemical condition of production. After adsorption of crude oil, aerogel floats to the top of the water surface, while granulated activated carbon sinks and settles on the bottom of the test bottle. The density of dried aerogel was measured after adsorption in two different configurations: in the packed column and in the bottle adsorption. They respectively were equal to 69.9 and 65.5 g/l. The increase in density was due to reduction of particle size and shrinkage of the aerogel network under the pressure of the slurry flow.

4.3.2. Aerogel Contact Angle

To indicate the hydrophobicity of aerogel granules, the contact angle of a small droplet of deionized water on the surface of aerogel was 151.2^{o} indicating a high degree of hydrophobicity of the surface (Figure 4.19). Previous contact angle data for this type of aerogel was not found in the literature or the product's specification sheet.

4.3.3. Crude Oil Retention Capacity of Adsorbents

Uptake of light and heavy crude oil by aerogel and granular activated carbon is presented in Figure 4.20. The aerogel uptake capacity for light and heavy crude oil was almost 5.5 to 8 times more than granulated activated carbon. Figure 4.21 indicates that the aerogel structure collapsed by adsorption of a high amount of adsorbate.

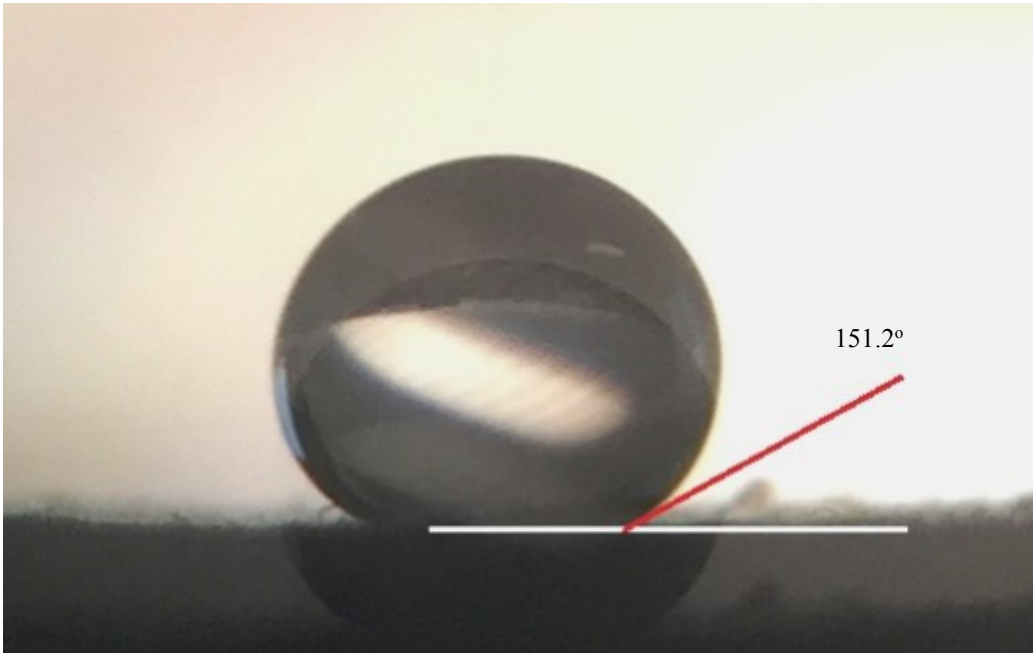


Figure 4.19. The contact angle of aerogel

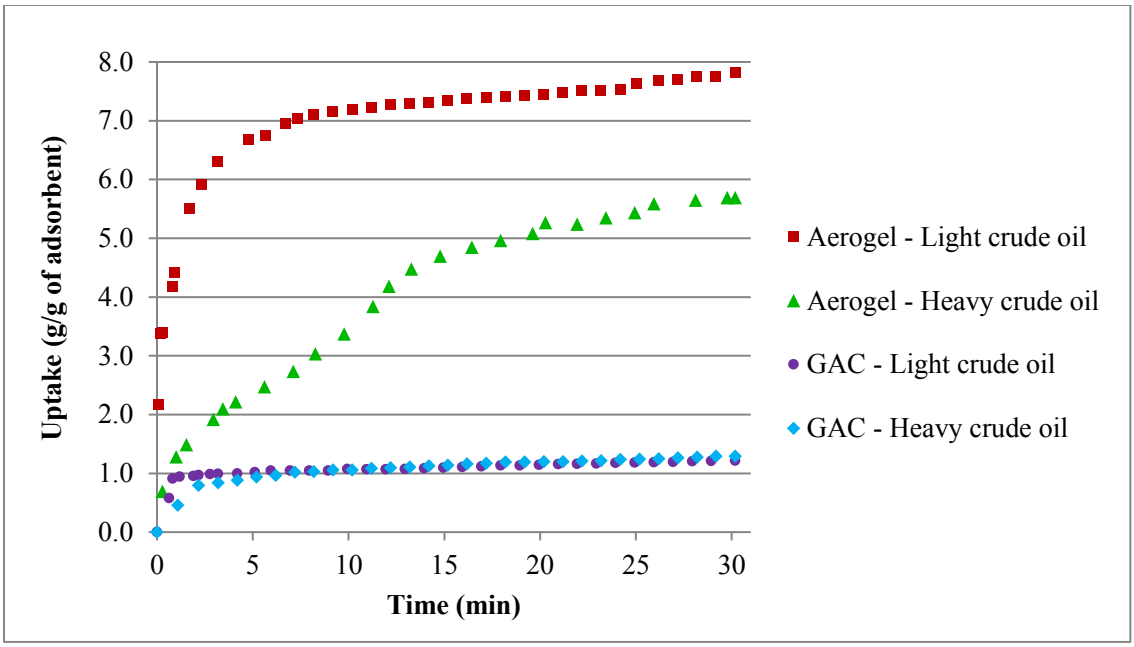


Figure 4.20. Uptake of light and heavy crude oil by aerogel and granulated activated carbon (values of duplicate measurements with ≤ 4% difference are presented)

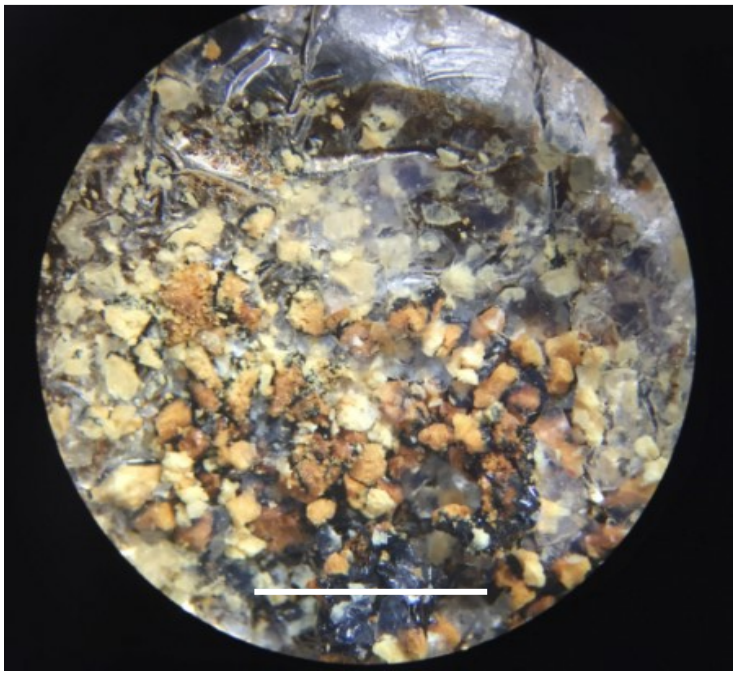


Figure 4.21. Adsorption of high amounts of crude oil by aerogel led to structure collapse; the bar represents 1 cm.

4.3.4. Uptake of Hydrocarbon by Adsorbent from Aqueous Phase

The uptake of TPH from water by aerogel and granular activated carbon is presented in Figure 4.22. In previous studies, GAC has been used as a reference for the demonstration of aerogel adsorption capacity (Hrubesh et al. 2001; Novak et al, 2005; Standeker et al., 2011; Wang, 2011). While for aerogel it took about 30 min to reach the final equilibrium concentration, for granulated activated carbon it was about 120 min. For an adsorbate initial concentration of 10 mg/l, the maximum adsorption capacity of aerogel was 9.6 mg/g for effluent concentration of 0.4 mg/l and for GAC was 3.3 mg/g for effluent concentration of 3.2 mg/l.

4.3.5. Adsorption kinetics

Two well-known kinetic equations including pseudo-first order and pseudo-second order (equations 2.5 and 2.6) were evaluated for fitting the adsorption data as represented in Figure 4.23. While the pseudo-second equation fits with a high degree of confidence, the pseudo-first order shows a small degree of consistency. Referring to Equations 2.6 and 2.7, the pseudo-second-order adsorption rate constant, k_2, and the theoretical adsorption capacity at equilibrium, q_e, were calculated respectively as 9.65 x 10^{-3} g/mg·min and 10.3 mg/g for aerogel.

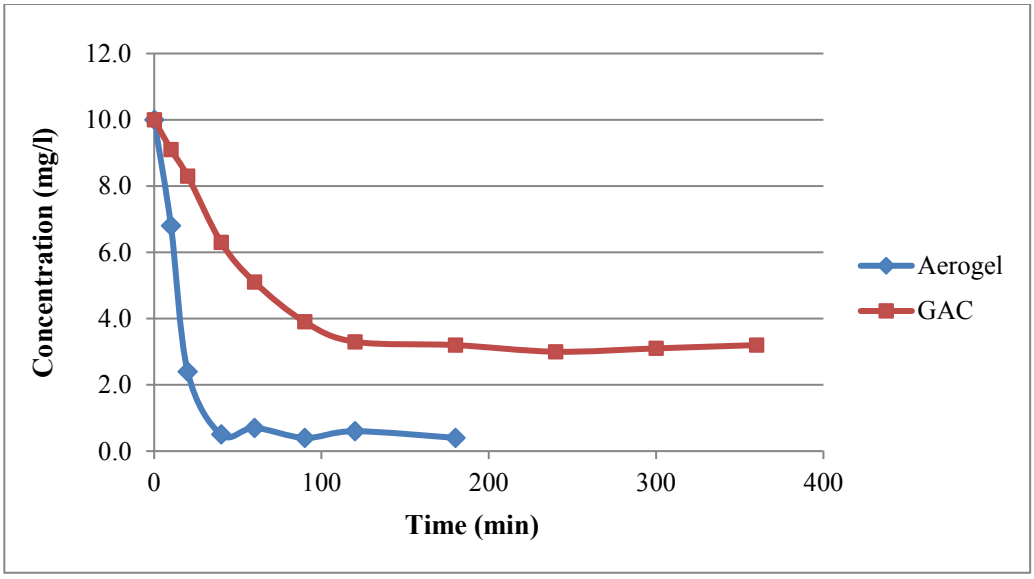


Figure 4.22. TPH adsorption from the aqueous phase by aerogel and granulated activated carbon

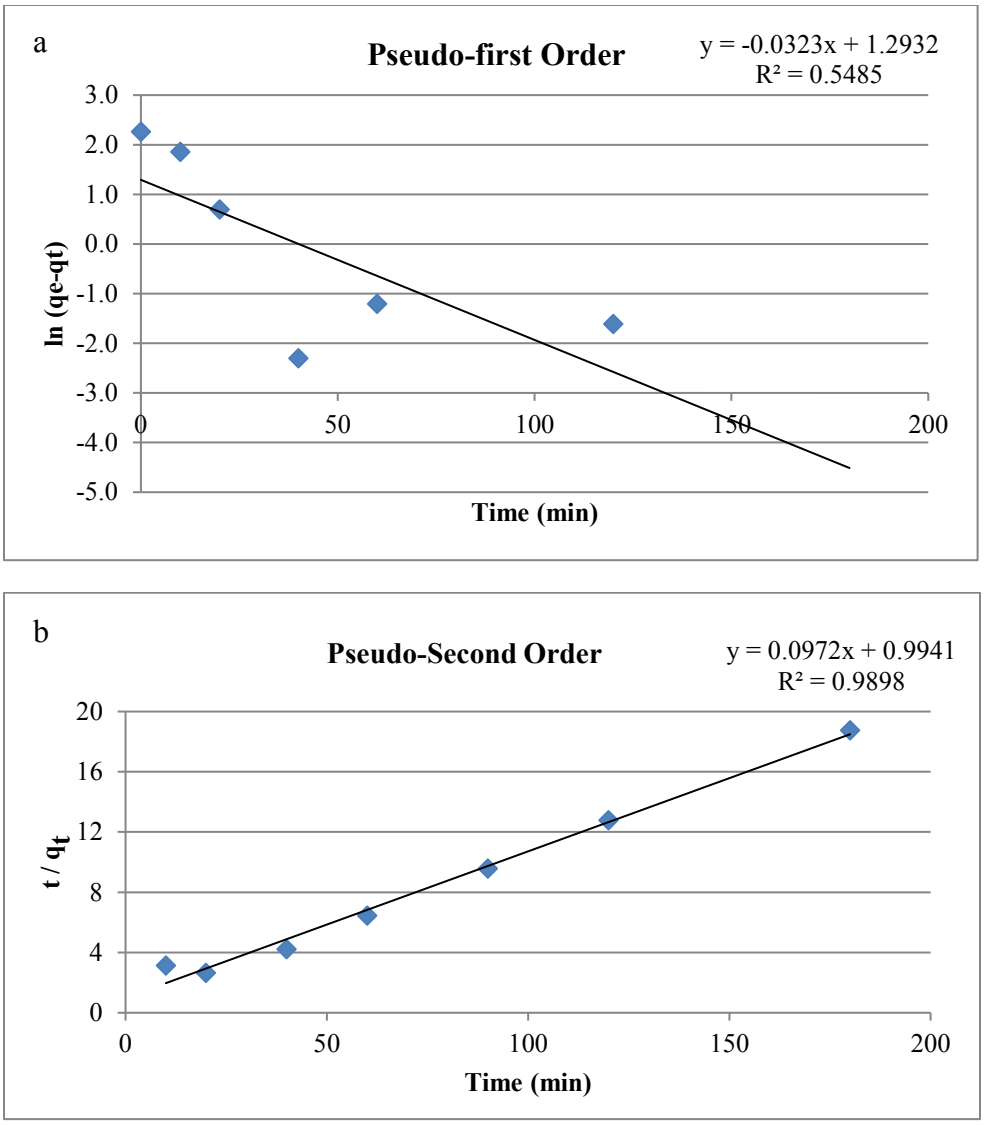


Figure 4.23. Aerogel adsorption data fitting for (a) pseudo-first order and (b) pseudo-second order mechanism

There are few studies on the kinetics of adsorption by silica aerogel. In a previous study by Abdoli et al. (2015), aerogel was used for adsorption of phenolic compounds from water. Adsorption data represented a better fit to pseudo-second-order kinetic rather than pseudo-first-order model. According to Ho & McKay (1998 & 1999), the pseudo-second order kinetics occurs when the chemical bonding between the adsorbent and adsorbate is due to forces stronger than physical attachment by van der Waals forces. The bonding in the pseudo-second order adsorption is similar to those of chemical bonds. Therefore, besides the diffusion of hydrocarbon into the porous

network of the aerogel granules, strong bonding exists as a part of the sorption mechanism. In chemisorption, the bonding step is a rate-controlling step rather than diffusion via the solid matrix. Chemisorption may be reversible or irreversible (IUPAC, 2001).

In previous studies (Liu et al., 2009; Standeker et al., 2007 & 2009; Venkateswara Rao et al., 2007), silica aerogels showed a significant adsorption capacity after 3 to 20 adsorption/desorption cycles, an indication of the reversibility of sorption. In the current study, when the silica aerogel was exposed to a pure hydrocarbon phase, deformation in the network structure was observed (Figure 4.21), while adsorption of a very low concentration of hydrocarbons from water did not show a visual detrimental effect on the structure of aerogel. As well, Fourier Transform infrared spectroscopy (FTIR) (section 4.3.10) did not indicate a significant change in the aerogel molecular structure after sorption of low concentrations of TPH from the water. Wang et al. (2005) showed that in sensors based on silica nanoparticle aerogel thin films, the mechanism of adsorption transferred from physisorption to chemisorption and the extent of reversibility changed at different ranges of concentration of the adsorbate.

4.3.6. Adsorption Isotherms

Adsorption isotherms including Langmuir (Equation 2.1) and Freundlich (Equation 2.3) isotherms for aerogel and granular activated carbon are shown in Figures 4.24 and 4.25. For both adsorbents, the adsorption of extracted TPH from sediment can be modeled by the Freundlich equation with a higher degree of reliability than the Langmuir equation. For the aerogel, Freundlich coefficients, k, and n were 4170 and 0.75 respectively and for granular activated carbon those are 160 and 0.66. The Freundlich isotherm is an empirical relation between the amount of adsorbate on the surface of an adsorbent to the concentration in the solvent; while the Langmuir is derived mathematically based on some limiting assumptions. For example, the Langmuir model assumes that an adsorbate behaves as an ideal gas at isothermal conditions. Also, it assumes that each site can hold only one molecule of the adsorbate and there is no interaction between adsorbate molecules attached on the surface of adsorbent. The Freundlich isotherm indicates a multi-layer sorption and takes the heterogeneity of adsorbate distribution into account (Wang, 2011).

Several previous studies showed that the Freundlich isotherm fits better than Langmuir isotherm to the behavior of silica aerogel for adsorption of hydrocarbons. For instance, Abdoli et al. (2015)

applied surface-modified silica aerogel for adsorption of phenolic compounds from aqueous solution. They concluded that Freundlich isotherm explains better the behavior of aerogel than the Langmuir isotherm. According to Novak et al. (2005), silica aerogel followed the Freundlich isotherm in adsorption of benzene, toluene, xylene and chloroform from water. In a study by Standeker et al. (2007) hydrophobic silica aerogel was applied for adsorption of chloroform, chlorobenzene, and dichloromethane, where the Freundlich model was governing the adsorption experiments. Wang (2011) concluded that the Freundlich isotherm fits better to the experimental data for adsorption of vegetable oil from water, for adsorption of oil from oily wastewater and for adsorption of VOCs in the vapor phase.

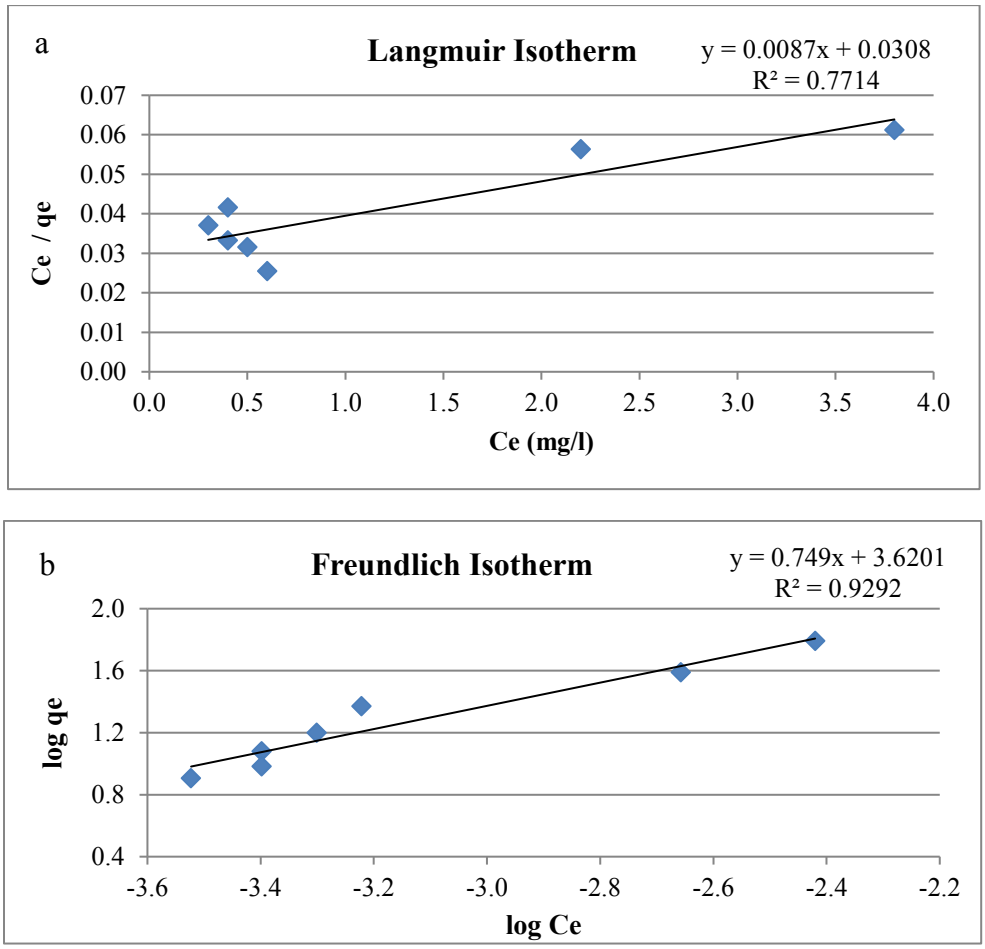


Figure 4.24. Fitted data for evaluation of (a) Langmuir and (b) Freundlich isotherm equations for aerogel

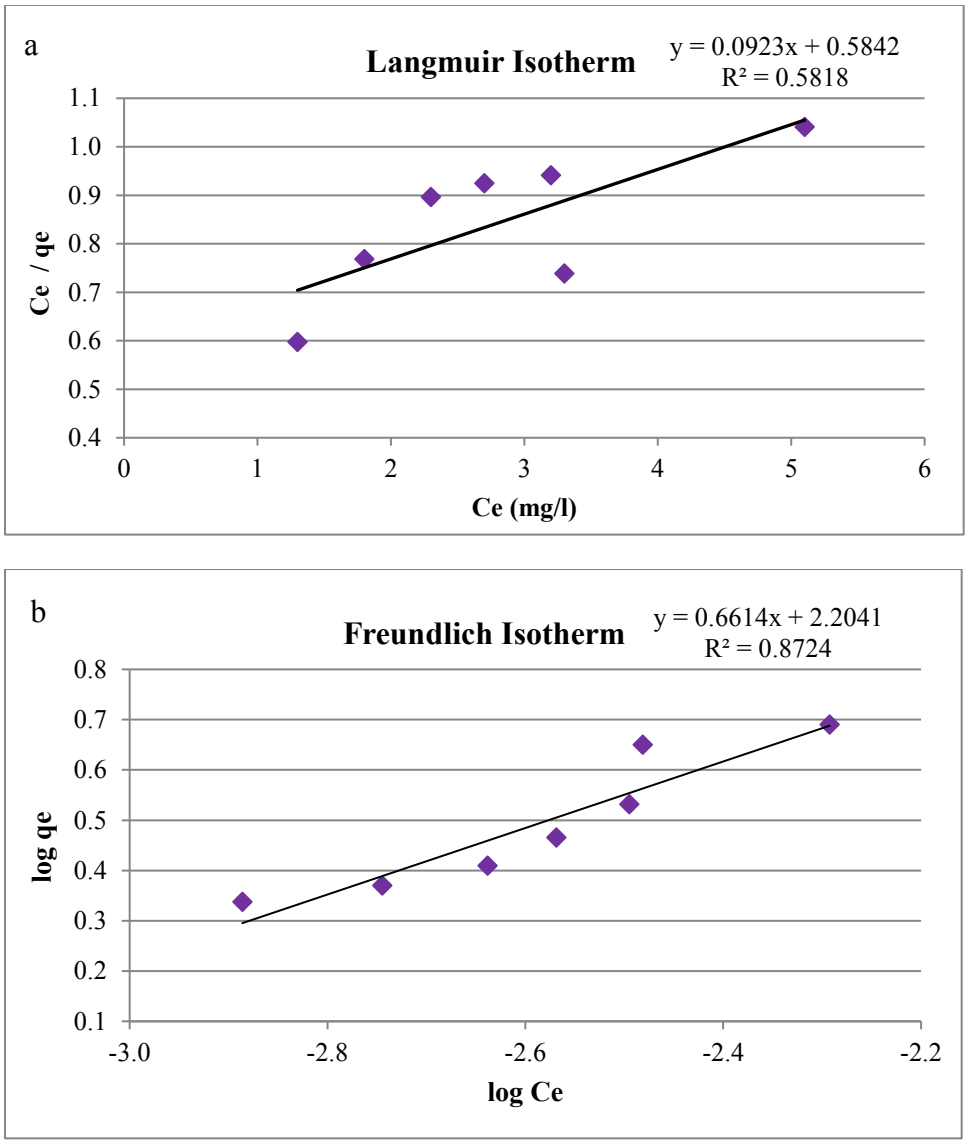


Figure 4.25. Fitted data for evaluation of (a) Langmuir and (b) Freundlich equations for GAC

4.3.7. Effect of pH on Adsorption by Aerogel

The effect of pH on the adsorption capacity of aerogel from 10 mg/l TPH in water emulsion is shown in Figure 4.26. At a pH below or above neutral, silica aerogel had a slightly lower performance for adsorption of TPH.

The better performance of aerogel at the neutral pH can be attributed to the lower stability of oil in water emulsions as well as higher hydrophobic nature of the hydrocarbon molecules. Strassner (1968) concluded that emulsions of crude oil in water with pH<5 were more stable than in

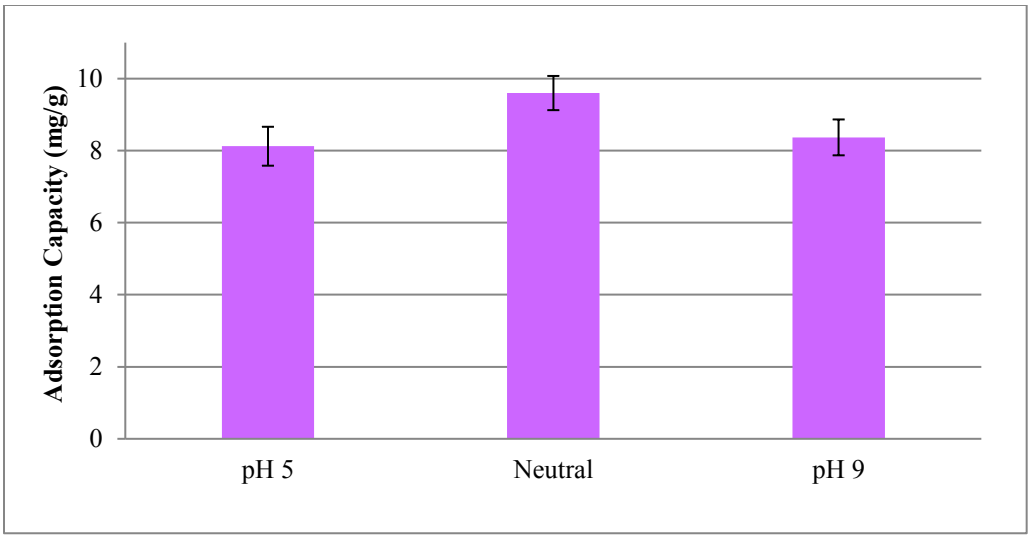


Figure 4.26. The effect of pH on the adsorption capacity of aerogel at $C_{initial}$=10 mg/l

neutral conditions. On the other hand, Daaou and Bendedouch (2012) showed that an Algerian crude oil emulsion was relatively stable at moderately basic pH. In a series of experiments on the adsorption of phenolic compounds from water by nanoporous silica aerogel, increasing pH from 7 to 9 decreased the adsorption capacity of aerogel (Abdoli et al. 2015). Poteau and Argillier (2005) showed that at pH lower and higher than neutral, the cationic and anionic charges made the hydrocarbon molecules to be ionized/polarized and consequently more hydrophilic. In a study by Franco et al. (2013), silica nanoparticles were used to adsorb crude oil from water. The time to reach adsorption equilibrium significantly reduced when pH increased from 5 to 7. Knapik and Stopa (2014) showed that a neutral pH was the best for adsorption of crude oil from water by a nanosilica adsorbent.

4.3.8. Effect of Temperature on Adsorption by Aerogel

The effect of temperature on the adsorption capacity of aerogel from 10 mg/l TPH in water emulsion is shown in Figure 4.27. By decreasing the temperature form 22 ^{o}C to 10^{o}C, no significant change was observed; while by increasing the temperature from 22^{o}C to 35^{o}C the aerogel adsorption capacity significantly decreased by 30%. By increasing the temperature, both

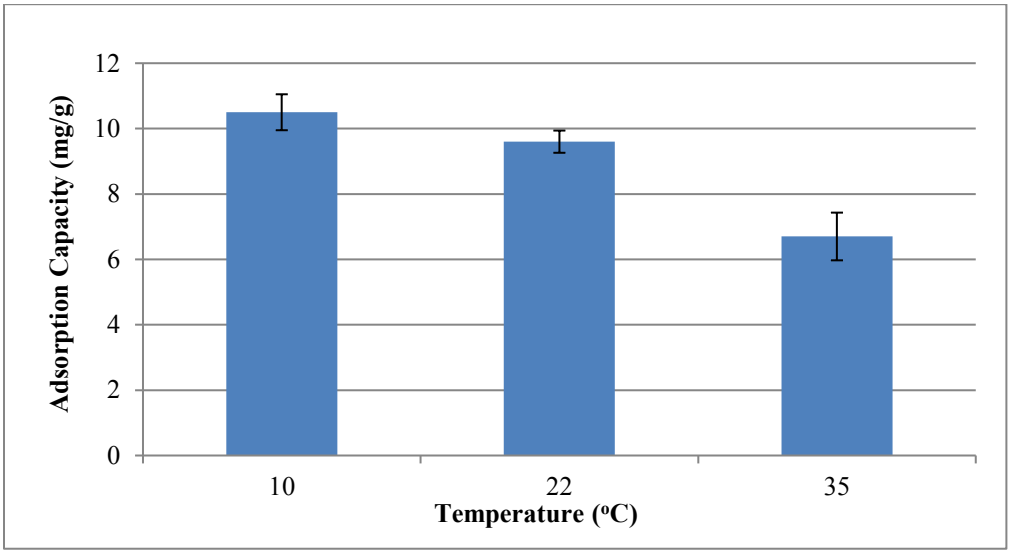


Figure 4.27. The effect of temperature on the adsorption capacity of aerogel at $C_{initial}$=10 mg/l

interfacial tension and viscosity decreased leading to an increase in solubility of hydrocarbons in water and stability of emulsion (Chang, 2016; Chen & Tao, 2005; Tadros, 2013). According to Chiou et al. (1979) for organic compounds, there is an inverse relationship between sorption coefficients and solubilities. Sheng et al (2010) reported that the adsorption capacity of silica aerogels decreased with the increase in temperature from 25°C to 65°C due to increasing nitrobenzene solubility in aqueous solution. According to Bayley and Biggs (2005), increasing the temperature decreases the hydrophobic properties of hydrocarbon contaminants and therefore reduces the potential energy holding the contaminants on the solid surface. Consequently, the required energy to remove the contaminants from the solid surface is less.

4.3.9. Electron Microscopy

Scanning electron microscopy (SEM) showed a rough surface with a large number of fractures on the surface of sediments after the desorption-sorption process in comparison with the sediments before the process (Figure 4.28). As well, for aerogels, the relatively smooth surface of granules became rough bearing cracks and fractures (Figure 4.29). The shear from sediment particles and water eddies caused the roughness on the surface.

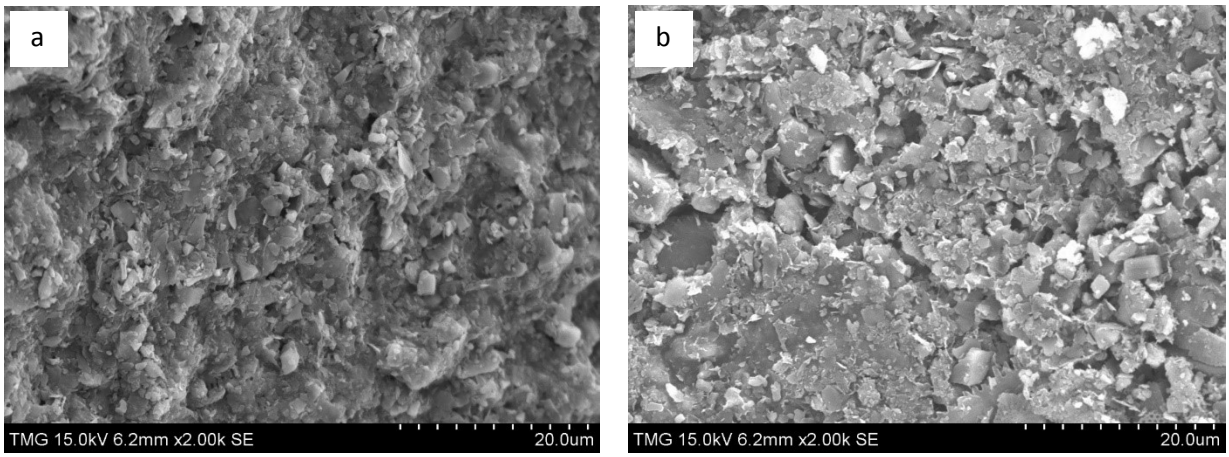


Figure 4.28. The appearance of the surface of sediment particles after the desorption-sorption process (b) in comparison with before the process (a)

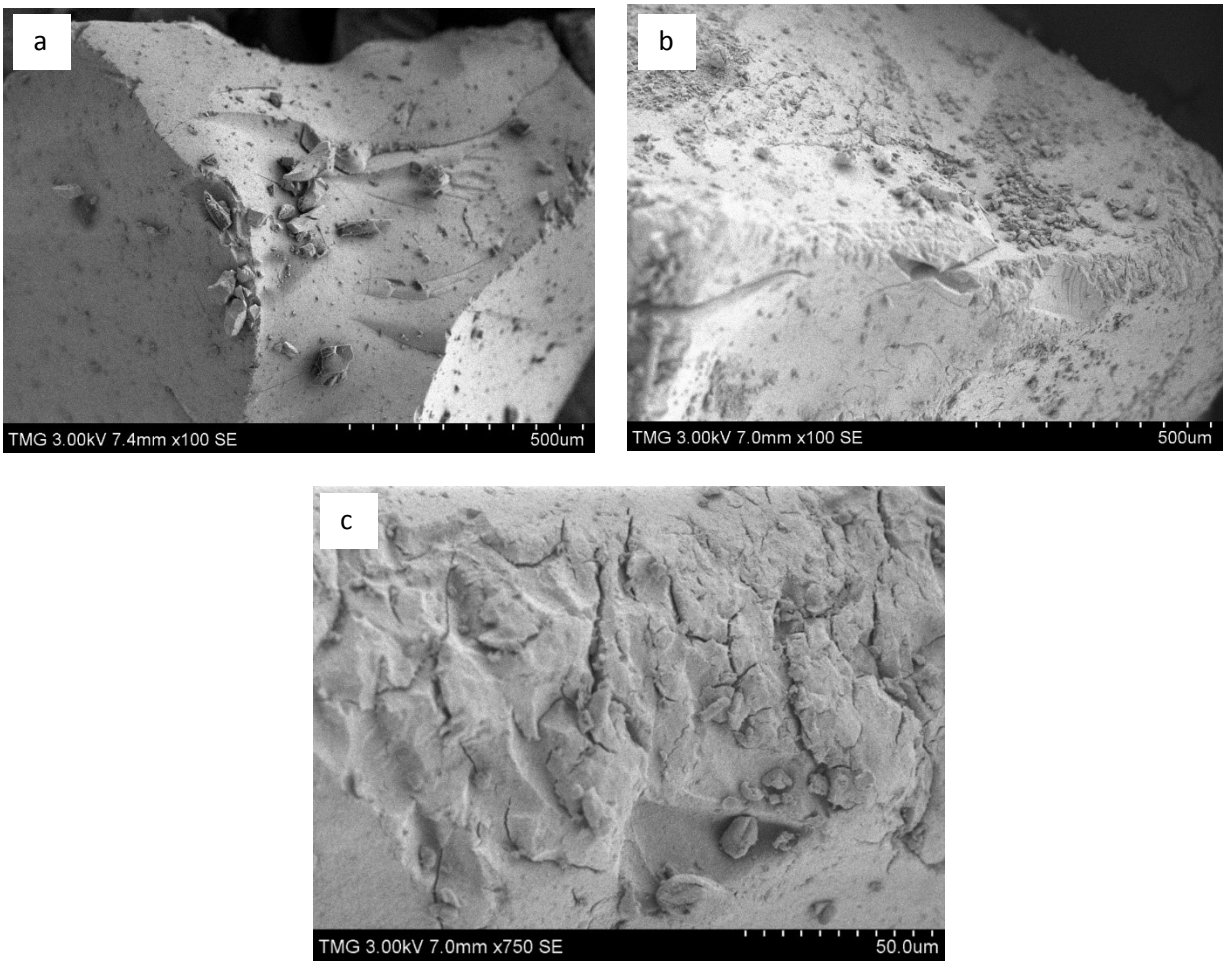


Figure 4.29. The appearance of the surface of aerogel particles (a) before and (b and c) after the desorption-sorption process

4.3.10. Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR spectrum of fresh aerogel and granules after desorption-sorption process are shown in Figure 4.30. Different bonds of Si-CH_3 formed 4 peaks in 755, 779, 797-815 and 1250±10 cm^{-1}. The peak at 2960 cm^{-1} indicated stretching vibration of both Si-C and C-H bonds. Si-O-Si bonding showed a peak in the range of 1020-1090 cm^{-1}. Si-OH bonding appeared in 950, 1610 and around 3650 cm^{-1}. A slight downward shift in the peaks after the desorption-sorption process for Si-CH_3 and Si-OH was observed (Al-Oweini & El-Rassy, 2009; Rytwo et al., 2015; Sarawade & Kim, 2007 & 2013).

4.3.11. Reuse of Aerogels

Previous research reported different capabilities for regeneration of silica aerogels, based on the surface modification methods. In a study by Perdigoto et al. (2012), the adsorption capacity of silica aerogel decreased by almost 50% after 3 cycles of regeneration. In another research by Standeker et al. (2009), the adsorption capacity of aerogel retained almost unchanged in at least 14 repeated cycles of adsorption/desorption. In a study by Liu et al. (2009), silica aerogel showed a stable adsorption capacity after 5 adsorption/desorption cycles. According to Venkateswara Rao et al. (2007), silica aerogels showed a significant adsorption capacity after 3 to 20 adsorption/desorption cycles.

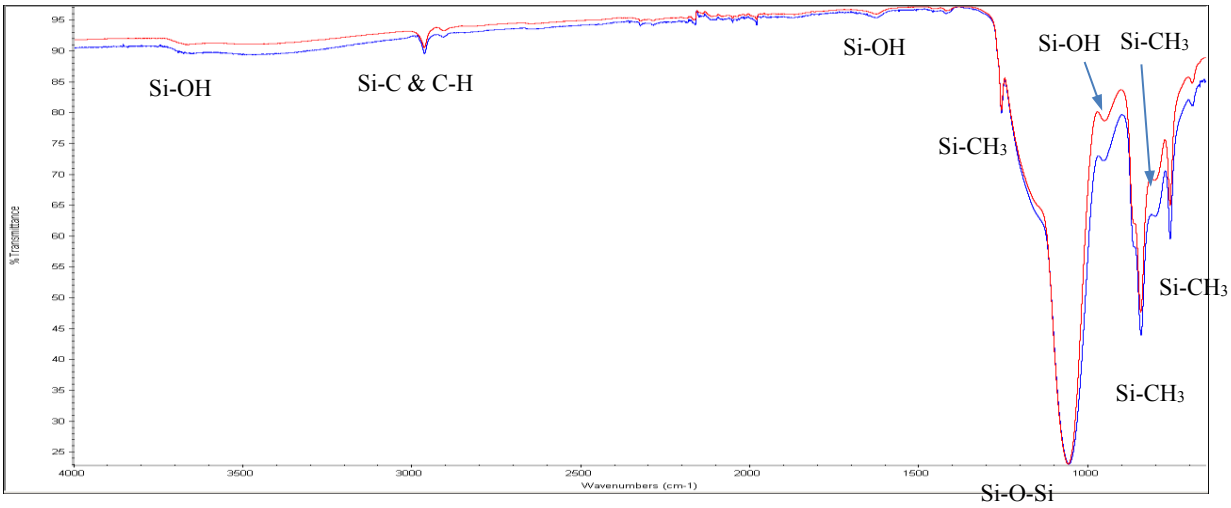


Figure 4.30. FTIR spectroscopy for fresh aerogels (red graph) versus processed aerogels (blue graph)

Regeneration by Solvent Experiments

The porous structure of aerogel particles collapsed after submerging in benzene, trichloromethane, dichloromethane, hexane, and acetone and drying in the ambient temperature (Figure 4.31). Observing the aerogel granules under a stereo-microscope revealed the fraction in the aerogels network (Figure 4.32). After drying, the capacity of aerogel particles for uptake of light crude oil was measured by applying the method explained in section 3.5.10. The results indicated that the sorption capacity of hydrophobic silica aerogels dramatically decreased after being submerged in hydrocarbon solvents (Figure 4.33). Fourier Transform Infrared Spectroscopy (FTIR) for fresh and dried solvent-submerged aerogels is represented in Figure 4.34. The downward shift before 1000 cm^{-1} in the peaks may indicate a change in the strength of bonds on the surface of aerogel particles. According to Venkateswara Rao et al. (2007), the shrinkage of aerogel granules might be due to the surface tension induced microfracture of the aerogel ligaments. As a result, the aerogel granules became brittle and shrank after total desorption of heavy hydrocarbons. The increased intensity of the C–H bonds around 3000 cm^{-1} possibly may be due to the presence of traces of hydrocarbon solvents in the aerogel samples.

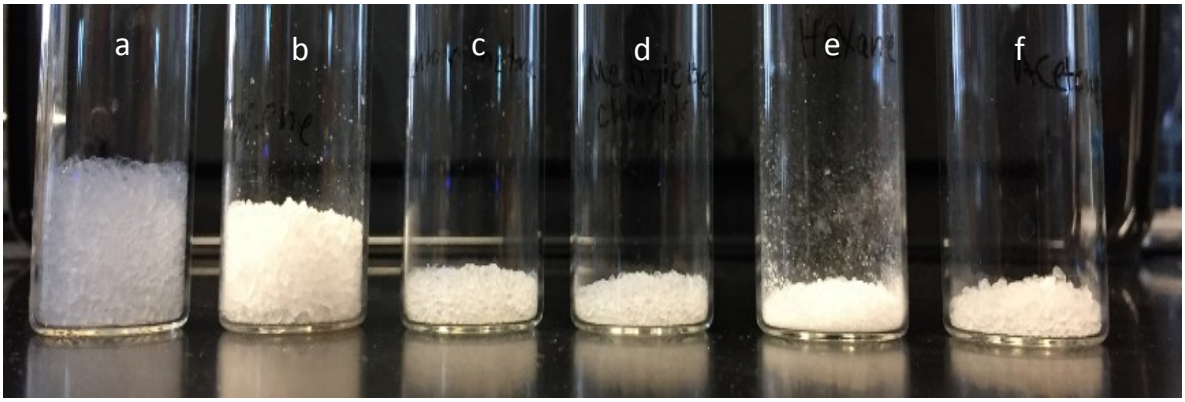


Figure 4.31. The porous network of fresh aerogel granules (a) collapsed after being submerged in various solvents: (b) benzene, (c) trichloromethane, (d) dichloromethane, (e) hexane and (f) acetone

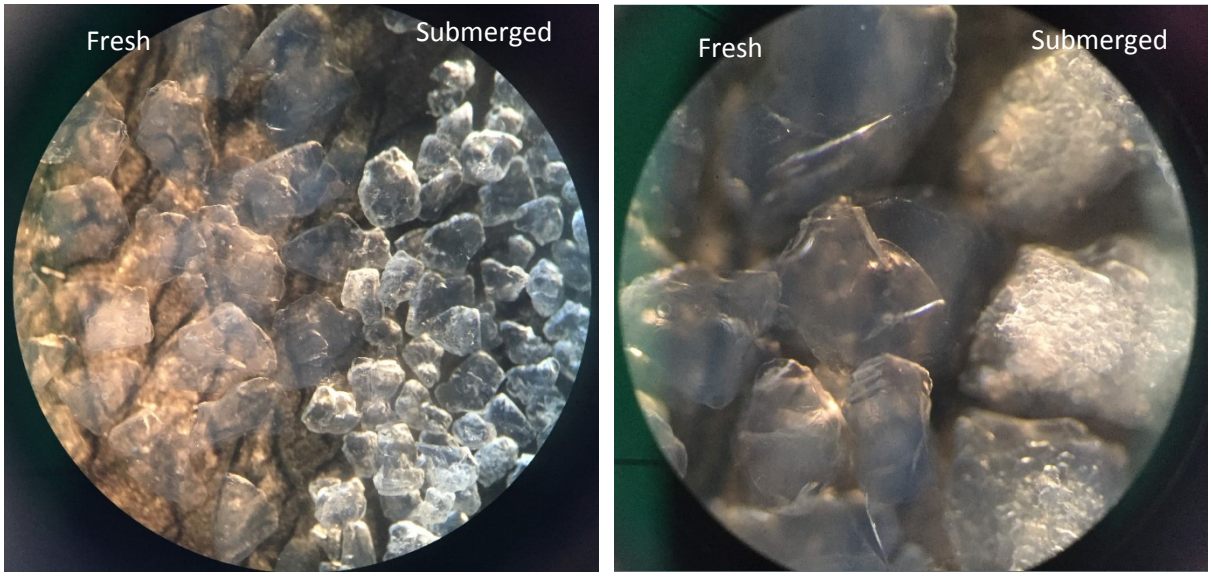


Figure 4.32. Shrinkage of aerogel granules and appearance of fractures in the aerogel network after being submerged in hydrocarbon solvents in comparison with fresh aerogel granules

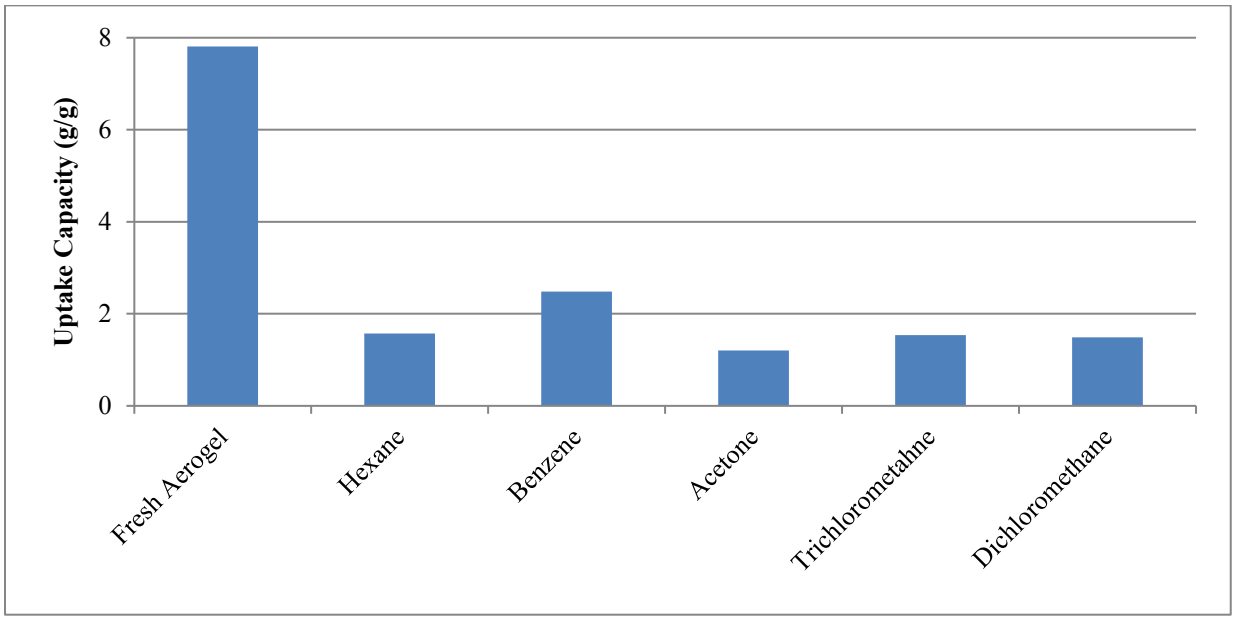


Figure 4.33. The capacity of fresh and submerged aerogels for uptake of various solvents

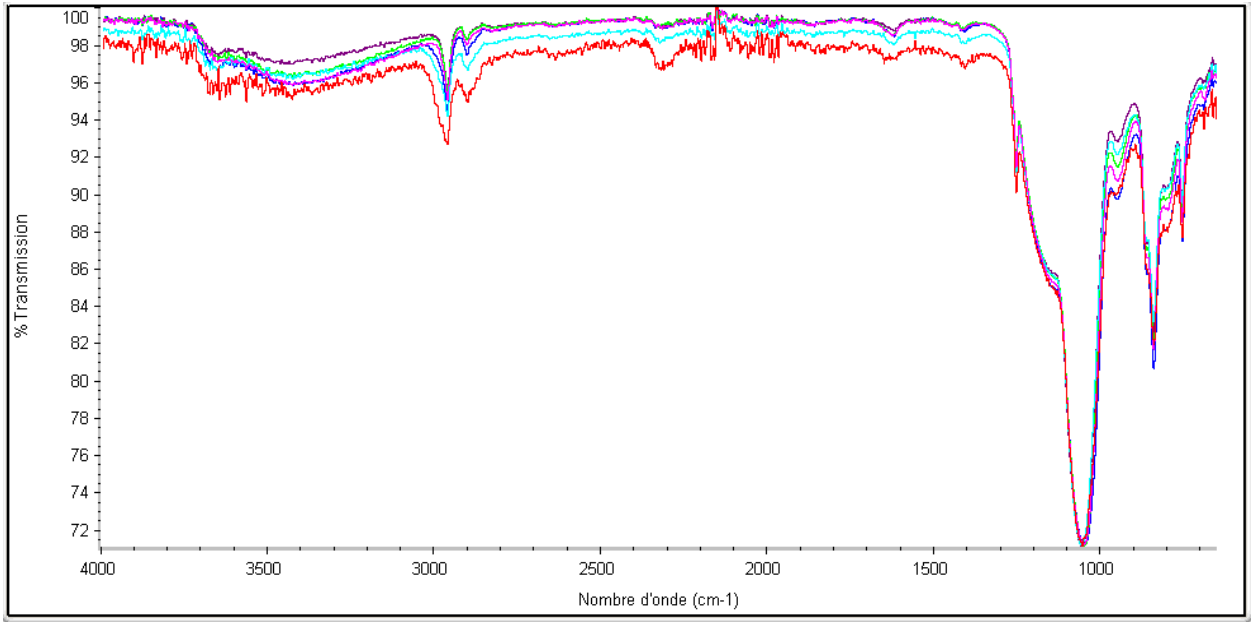


Figure 4.34. Fourier Transform Infrared Spectroscopy (FTIR) for fresh aerogels (violet) and submerged in benzene (green), hexane (purple), acetone (dark blue), dichloromethane (cyan) and trichloromethane (red)

Regeneration by Heat Experiments

The results of thermogravimetric analysis (TGA) experiments showed that starting from ambient temperature up to about 300ºC, there was no significant change in the weight of aerogel granules. From 300ºC, the weight of aerogel particles started to decrease and around 400ºC there was a sharp reduction in the weight, indicating decomposition of methyl groups in aerogel network (Figure 4.35) (Shewale et al., 2008).

According to the gas chromatographic results, the highest boiling temperature for this range was 265ºC for C36 (hexatriacontane). The preliminary regeneration tests by heat were conducted at three temperatures of 200, 250 and 300ºC. To evaluate the effect of various regeneration temperatures on the structure of hydrophobic silica aerogels, Fourier transform infrared spectroscopy (FTIR) was performed. The results indicated that by increasing the regeneration temperature, there was a downward shift for peaks under 900 cm^{-1}. Also, peaks appeared or grew at 1400, 2900, 2960 and 3660 cm^{-1} indicating C-H, C-H, C-H and O-H bonds, respectively. The downward shift may be attributed to a change in aerogel functional groups(Figure 4.36) (Perdigoto et al., 2012; Poiana et al, 2015; Venkateswara Rao & Kulkarni, 2002). To minimize the

decomposition of oxy-tri-methyl-silyl groups in the aerogel network, the temperature of 200ºC was selected for heat-regeneration tests.

The results for investigating the best regeneration time-length indicated that before 30 minutes the weight loss stopped. Therefore, 30 minutes was selected for the aerogel regeneration time by heat (Figure 4.37).

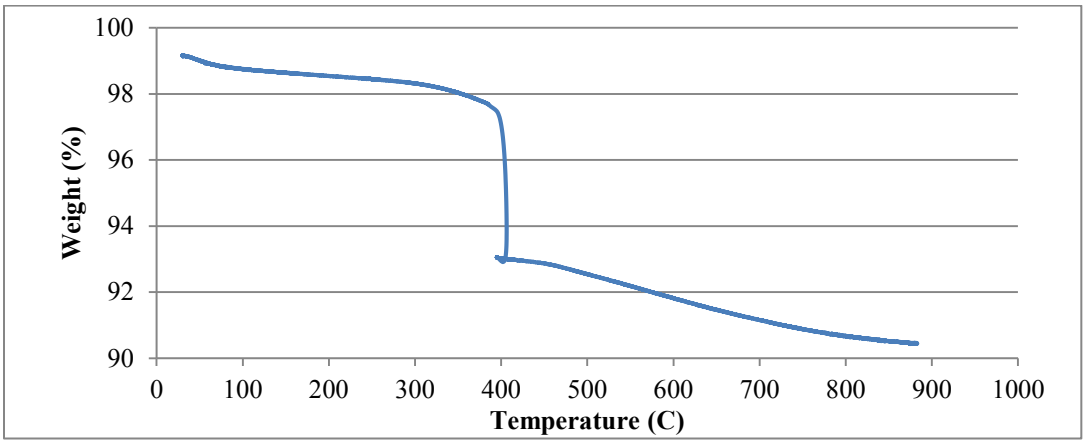


Figure 4.35. Thermogravimetric analysis (TGA) of aerogel granules

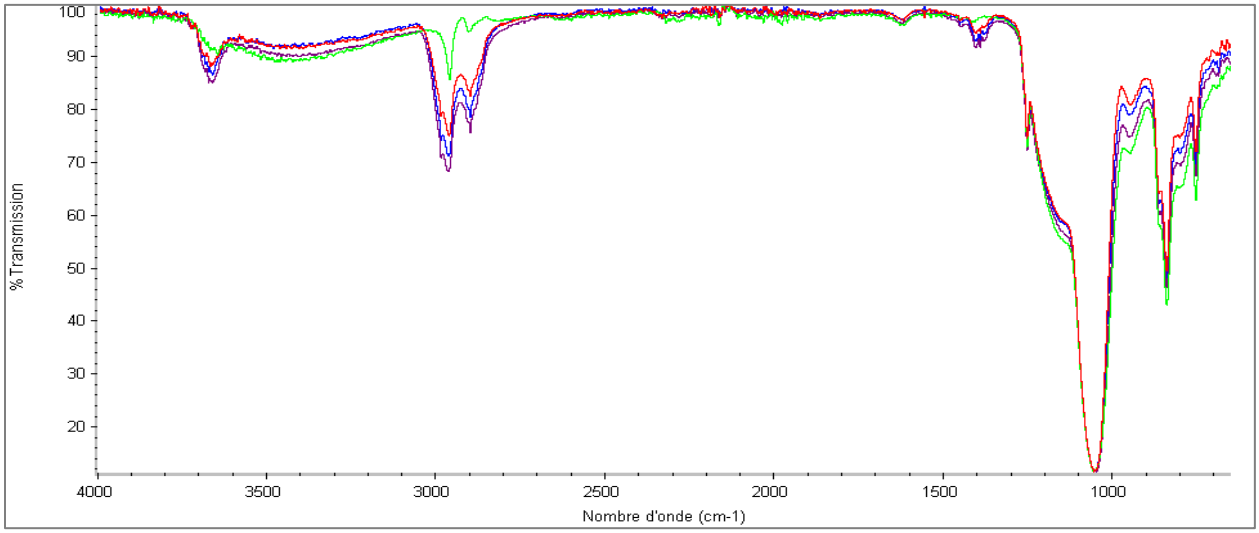


Figure 4.36. FTIR for used not-regenerated aerogel (green), regenerated at 200 ºC (red), 250 ºC (blue) and 300 ºC (purple)

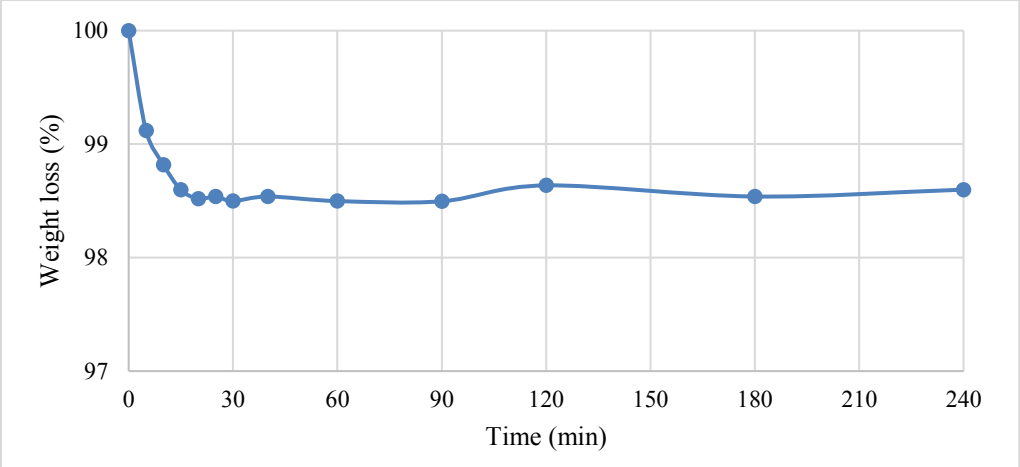


Figure 4.37. Aerogel granule weight loss at 200°C

The result of regeneration experiments for different cycles is presented in Figure 4.38. The adsorption capacity of aerogels decreased about 7% after 2 cycles of regeneration but dropped significantly from the third cycle by 25%. FTIR spectroscopy of regenerated aerogels revealed a more intensive change in functional groups in the aerogel network by increasing the regeneration cycles after the 2nd cycle (Figure 4.39), resulting in the decrease in the reduction of sorption capacity. At the industrial-scale the hydrocarbon vapors need to be collected and used aerogels will need to be managed properly to avoid air pollution.

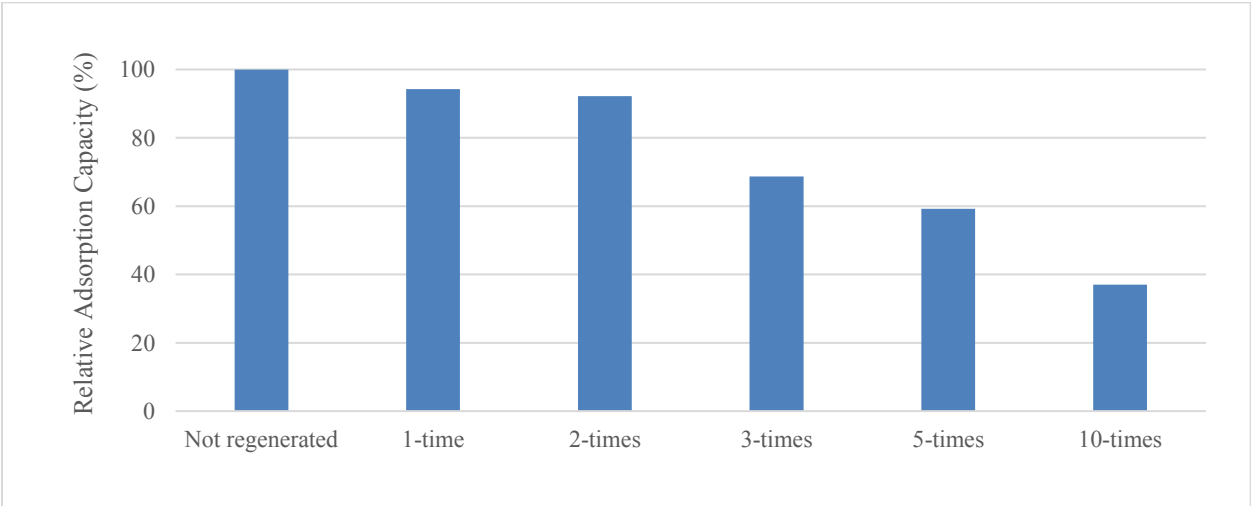


Figure 4.38. The adsorption capacity of silica aerogel after different cycles of regeneration by heat at 200°C

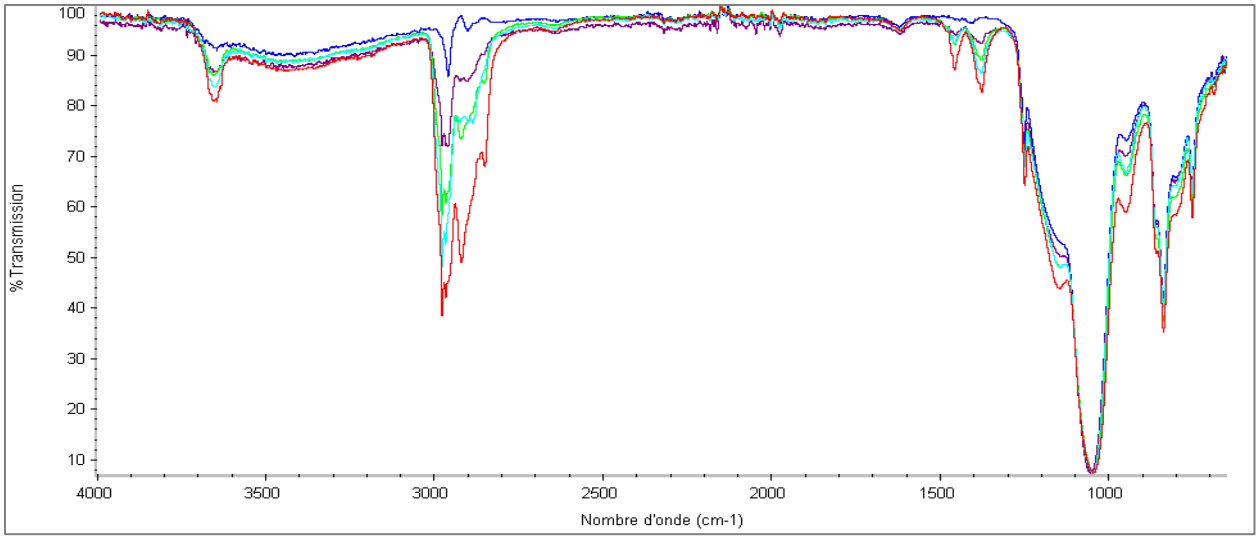


Figure 4.39. FTIR, not regenerated (dark blue), regenerated 1 time (purple), 3 times (green), 5 times (cyan) and 10 times (red)

4.4. Power Consumption

4.4.1. Gas Hold up and Hydraulic Retention Time (HRT)

The working volume of the liquid in the mixer was 860 ml and the agitated gas-liquid-solid was 1700 ml. According to the method explained in section 3.5.17, the average hydraulic retention time was calculated as 11.5 seconds. The gas hold-up was calculated as 50.6%.

4.4.2. Power Consumption in Sorption-Desorption Setup

Power consumption for different impeller rotation speeds was calculated based on Equation 3.6. The results are represented in Figure 4.40. The extent of remediation is shown on the same graph indicating the existence of consistency between mixing power and remediation of the sediment. The system was gassed, with more than 50% of the gas holdup. The power equation depended only on the density of the gassed slurry. Power number (Np) was constant as the pattern was turbulent. The correlation equation between remediation and agitation speed can be expressed by linear Equation 4.1 in which P is power (kW) and r is the efficiency of total petroleum hydrocarbon remediation (%). The coefficient of correlation (R^2) was 0.989, indicating a high degree of linear-fitting regression.

$$P = 0.036\ r - 0.5689 \qquad \text{Eq. 4.1}$$

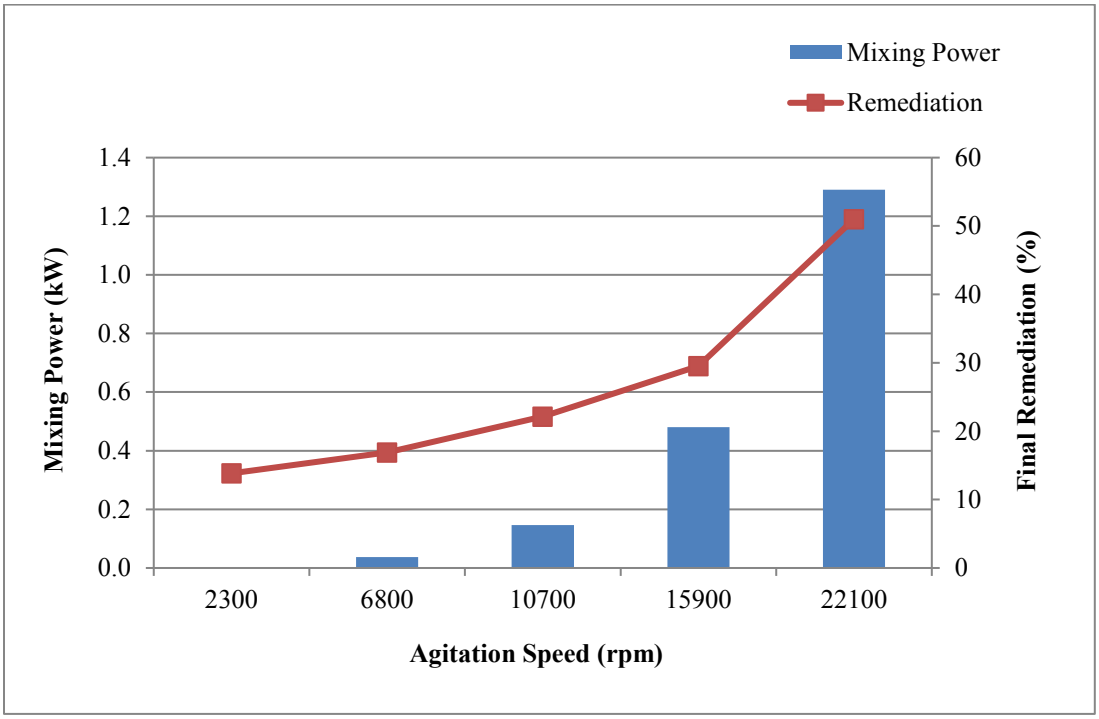


Figure 4.40. Mixing power and remediation extent versus the rotation speed of the impeller

Comparison these results with Figure 4.41 indicates that with the agitation speed at 15900 rpm, the effluent sediment is compliant with the federal and provincial thresholds. Increasing the agitation speed to 22100 rpm increases the extent of remediation by 73% and the power consumption by 1.7 times, which may not be necessary.

4.5. Sediment Quality

According to the previous analysis, the sediment samples did not contain PCBs or pesticides (Alavi, 2011 & Exova analysis). Therefore, the sediment quality evaluation concentrated on the content of hydrocarbons, heavy metals, phosphorus, and nitrogen.

4.5.1. Efficiency of the Desorption-Sorption Process

Figures 4.41 and 4.42 represent the final reduction in the TPH content of contaminated sediments and effluent water. The results are compared with Canadian federal and provincial (Ontario and Nova Scotia) criteria for sediment and water quality. The initial comparison to regulatory levels has been discussed earlier in the characterization section (4.1.4) to show the need for remediation.

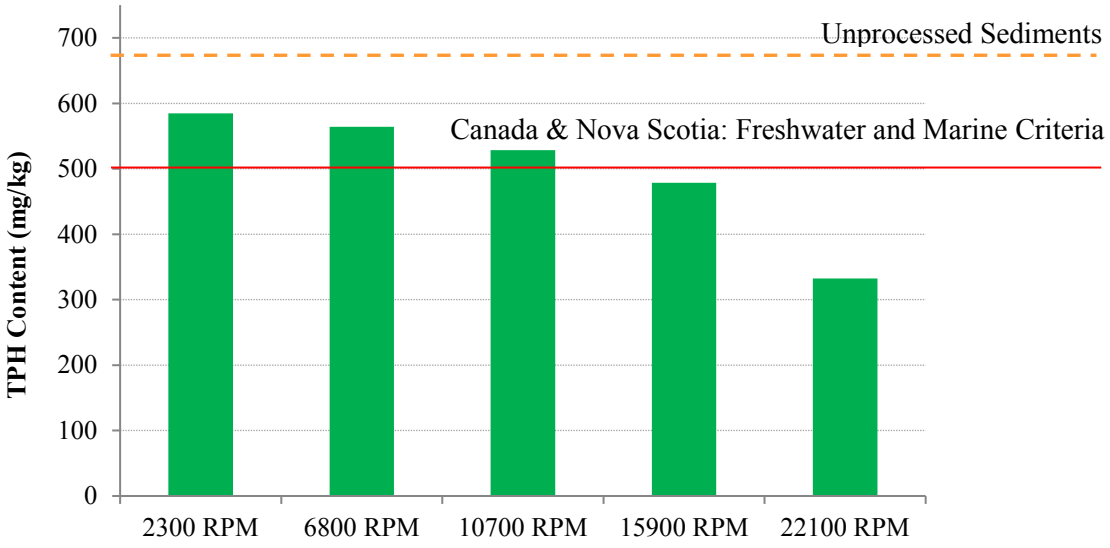


Figure 4.41. TPH Concentration in sediment after a 3-hour process (45 min agitation)

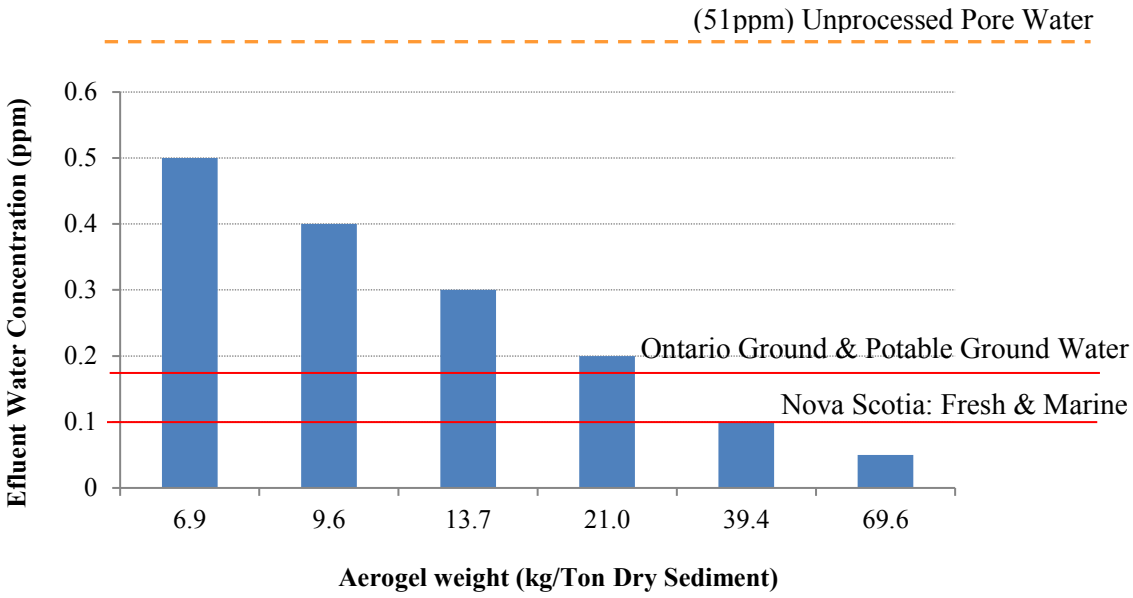


Figure 4.42. Effluent water by applying aerogel for a 10 kg/m^3 sediment load

4.5.2. Heavy Metals

The content of heavy metals in the sediment samples before the desorption-sorption process are represented in Table 4.1 accompanying with rare effect level (REL), threshold effect level (TEL), occasional effect level (OEL), probable effect level (PEL) and frequent effect level (FEL). When the concentration of a heavy metal is higher than the OEL but lower than or equal to the FEL the probability of causing adverse biological effects is relatively high. When the concentration is greater than the FEL, the probability of causing adverse biological effects is very high (Environment Canada & Ministère du Développement durable, de l'Environnement et des Parcs du Québec, 2007). Therefore, the riverbed where the sediment samples were taken needed to be remediated. The concentration of heavy metals in the solid portion of the sediments after being exposed to a vigorous agitation did not show a significant change, indicating that strong turbulence in a short time was not enough to extract the heavy metals from sediments by-itself.

Table 4.1. Content of selected heavy metals in sediment samples used in this study and sediment quality criteria. The blank spaces indicate no data is available (Environment Canada & Ministère du Développement durable, de l'Environnement et des Parcs du Québec, 2007).

Heavy Metal	Concentration (mg/kg dry basis)	REL	TEL	OEL	PEL	FEL
Cr	150.05	25	37	57	90	120
As	10.50	4.1	5.9	7.6	17	23
Cd	2.01	0.33	0.60	1.7	3.5	12
Pb	138.79	25	35	52	91	150
Cu	320.35	22	36	63	200	700
Zn	641.92	80	120	170	310	770
Ni	45.38			47		
Mn	758.57					
Co	13.49					
Mo	2.34					

Previous studies have shown that silica aerogel granules are able to adsorb some heavy metals. Maleki (2016) reviewed the studies on the application of aerogels in heavy metal removal from water. Shokouki et al. (2010) used silica aerogels for heavy metal removal. Aerogel showed the capability of adsorption for Cd^{2+}, Ni^{2+}, Pb^{2+} and Zn^{2+} cations from aqueous solutions as large as 35.71, 40.00, 45.45 and 34.48 milligrams per gram of aerogel, respectively. Figure 4.43 represents the measured concentration of heavy metals in the desorption-sorption process water at the beginning of experiments, after 3 hours of residing in the desorption-sorption process as well as after 3 hours of agitation (including 20-second agitation and 60-second rest cycles). The concentration of heavy metals in the process water (10 g/l sediment in water slurry) was in the order of a part per billion. The hydrophobic silica aerogel used in this study could remove heavy metals from the solution between 2.3% (for cadmium) up to 65.1% (for lead). The capacity of aerogels, similar to any adsorbent, for adsorption of heavy metals depended on the concentration of metallic ions in the solution as well as functional groups at the surface of particles. The surface of the hydrophobic aerogel particles had strong hydrophobic bearing $C\text{-}(CH_3)_3$ functional groups which obviously could not be considered as a good sorbent for removal of ionic metals. As Table 4.2 represents, the final concentrations of heavy metals in the desorption-sorption process water were significantly lower than the allowed concentrations by Quebec and Canada drinking water quality criteria.

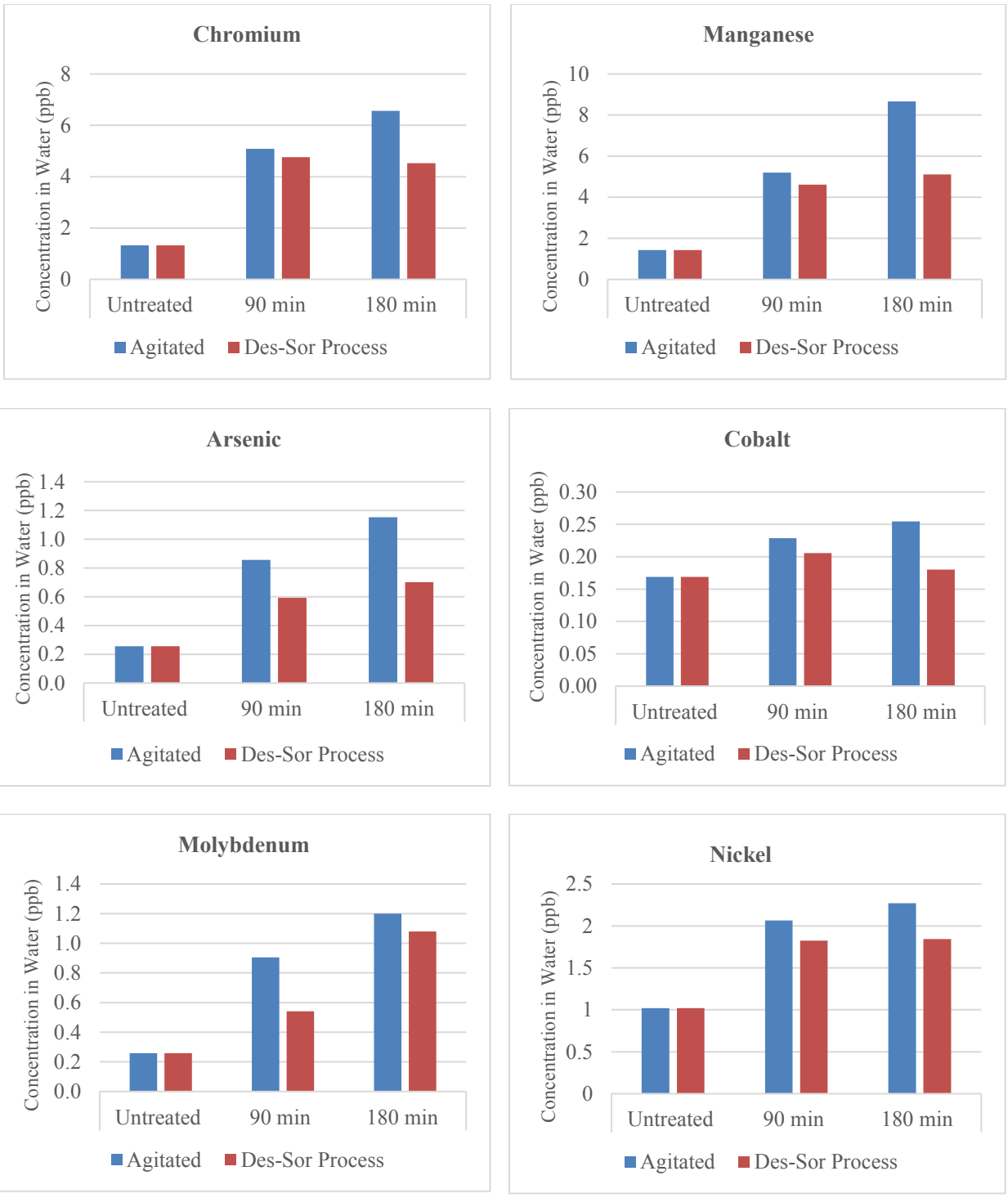
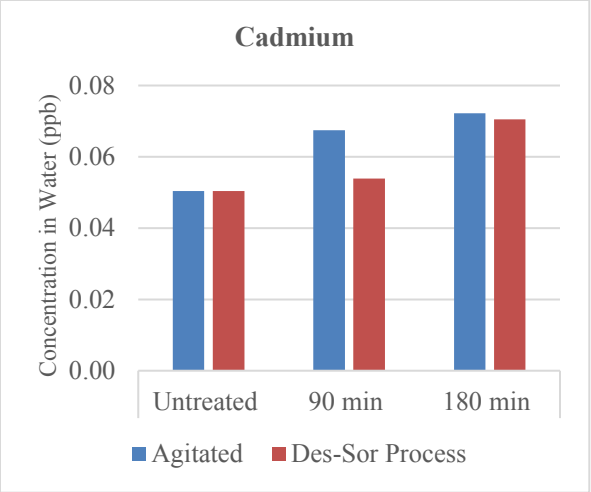
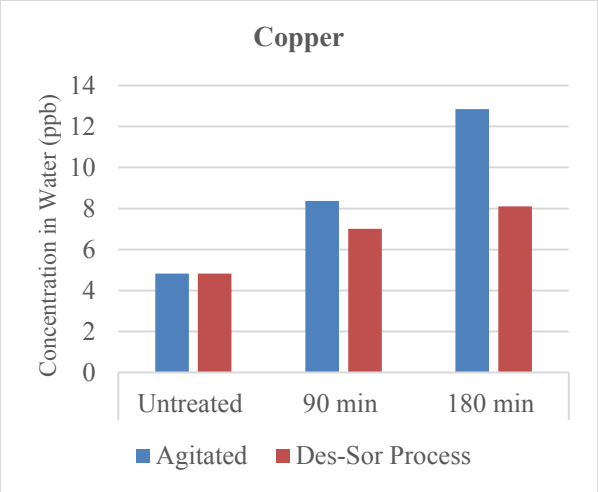
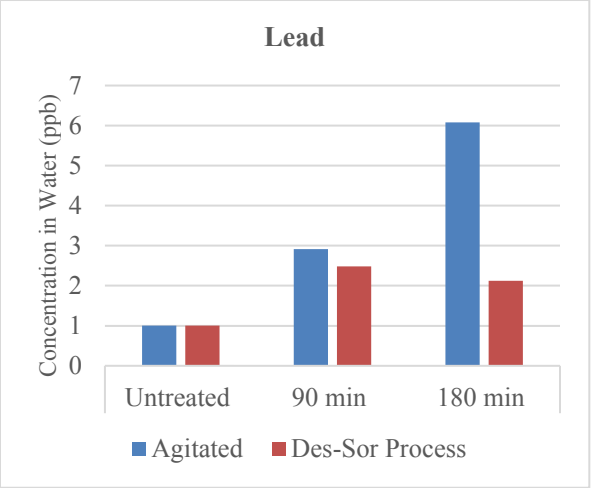


Figure 4.43. Concentration of selected heavy metals in process water during agitation and desorption-sorption process (the figure is continued on the next page)







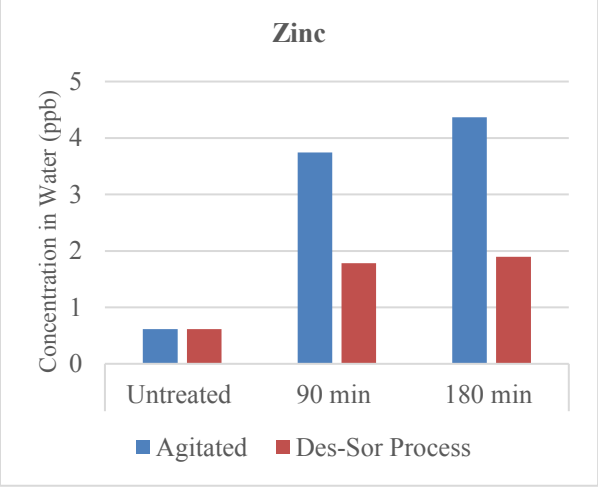


Figure 4.43. (continued)

Table 4.2 Quebec and Canada drinking water quality criteria, the final concentration of heavy metals in desorption-sorption process water and removal percentage by hydrophobic silica aerogels

Heavy Metal	Maximum Allowed Concentration(mg/l) in Quebec & Canada	Final Concentration in Desorption-Sorption Process Water (mg/l)	Removal from Water (%)
Pb	0.01 & 0.05	0.0021	65.1
Zn	No data & 5.0	0.0019	56.6
Mn	& 0.05	0.0051	41.0
As	0.01 & 0.05	0.007	39.1
Cu	1.0 & 1.0	0.0081	37.0
Cr	0.05 & 0.05	0.0045	31.1
Co	No data & 0.05 (irrigation)	0.0002	29.3
Ni	No data & 0.2 (irrigation)	0.0018	18.8
Mo	No data & 0.01 (irrigation)	0.001	9.9
Cd	0.005 & 0.005	0.0001	2.3

4.5.3. Phosphorus

Removal of phosphorus from water or wastewater by adsorption has widely been studied (Chad et al., 2017; Kumar et al., 2014; Mengxue et al., 2016; Peleka & Deliyanni, 2009). Tran et al. (2015) used graphene–nanoparticle aerogel composites with a capacity of 350 mg/g to remove phosphorus from water at an initial phosphate concentration of 200 mg/l.

The concentration of total phosphate in water after being exposed to a vigorous agitation and desorption-sorption process is presented in Figure 4.44. In the desorption-sorption process, the final concentration of phosphorus after 3 hours was 65% less than an only-agitation process, while aerogel was absent. The surface of hydrophobic aerogels used in this study contained CH_3 functional groups. Luo et al. (2016) studied the adsorption of phosphorus from water using zirconium-loaded graphene oxide with CH_3 functional groups. They reported that the adsorption

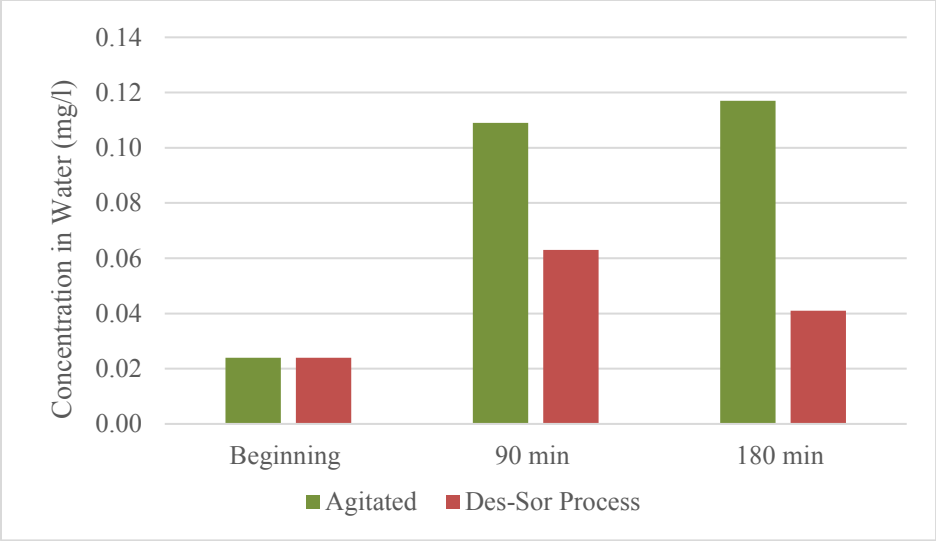


Figure 4.44. The concentration of total phosphate in process water during agitation and desorption-sorption process

kinetics followed pseudo-second-order kinetics and a Langmuir isotherm with maximum adsorption capacity of 27.71 mg/g. The content of phosphorus in the solid portion of sediments samples (1186 mg/kg) did not change significantly, indicating a strong bond between phosphorus and sediment particles.

4.5.4. Nitrogen

The concentration of total nitrogen, including total Kjeldahl nitrogen (TKN) and inorganic nitrogen (NO_3^- and NO_2^-), in process water during the desorption-sorption and only-agitation process (in the absence of aerogel) is represented in Figure 4.45. The presence of aerogel did not affect the concentration of inorganic nitrogen, indicating that hydrophobic silica aerogel did not have an affinity toward inorganic nitrogen. The concentration of total Kjeldahl nitrogen (which is the total of organic nitrogen and ammonia) in the absence of aerogel was very low. After 3 hours of the desorption-sorption process, the reduction in TKN concentration was more than 95%, with the final concentration of under the limit of detection of the applied measurement method (Hach TNT 880).

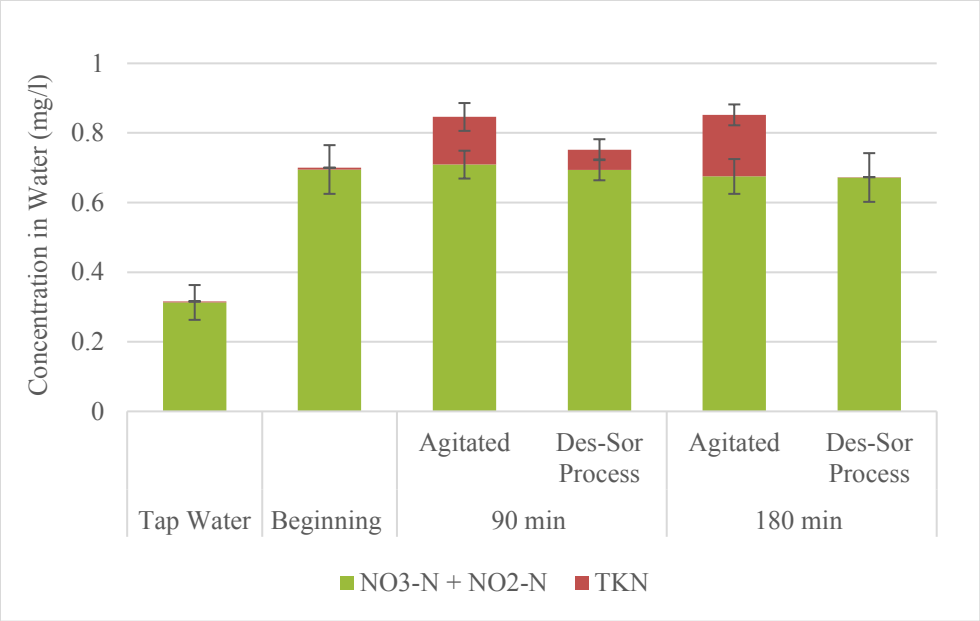


Figure 4.45. The concentration of total nitrogen (including total Kjeldahl nitrogen and NO_3-N + NO_2-N) in process water during agitation and desorption-sorption process

Basiuk and Gromovoy (1996) studied the adsorption of amino acid from water on bare and octadecyl-functionalized silica ($[SiO]_x$–$[CH_2(CH_2)_{16}CH_3]_y$). They concluded that ionic interaction was the main mechanism for the adsorption on bare silica, whereas both hydrophobic interactions with octadecyl groups on silica and ionic interactions with silanol groups ($(CH_3)_3Si$–OH) governed the adsorption on octadecyl-functionalized silica.

4.6. Desorption-Adsorption Mechanism

Desorption of contaminants from sediment particles

In previous research, fluorescence microscopy imaging has been used to study oil-suspended particulate matter aggregates (OMA) (Khelifa et al, 2005; Sun et al., 2014). In the present research, fluorescence microscopy showed a reduction in distribution and size of oil particles in the sediments. Scanning electron microscopy analysis (SEM) performed for investigating the morphology of sediment after the desorption-sorption process showed the attrition and wearing of the surface of sediments. On the other hand, particle size analysis indicated that the size of the

sediment particles was reduced from 3.7-5.7 µm for unprocessed sediment to 0.69-0.75 µm for processed sediments resulting in more exposed surface area to the turbulence flow. According to Jiang et al. (2009), a vigorous agitation creates collisions and frictions between particles, themselves and the impeller, leading to abrasion, scrubbing, scouring and particle disintegration. This condition results in the liberation of the contaminants into the surrounding environment (Figure 4.46 a to c).

Jobin et al. (2015) applied attrition for decontaminating contaminated soil by heavy metals. They concluded that the reduction in particle size, scrubbing the surface and loosening the bonding leads to decontamination of soil. According to Bayley & Biggs (2005a), three forces potentially bind the contaminant to the surface of the sediment particle:

i. The existence of chemical bonds between solid and contaminants e.g. chemical reactions of contaminants and organic matter on the surface of the particle.
ii. Hydrophobic/hydrophilic characteristics (solubility) of the contaminants
iii. Physical forces between contaminants and the surface of the solid (van der Waals).

In the attrition of contaminated solids, because of the physical impact, contaminated particles are either detached from the surface of a larger particle or the bonds between the contaminants and the particle surfaces are sufficiently weakened to some extent to be broken by further impact. According to the soil aggregate hierarchy theory, breakdown happens when sufficient mechanical stresses can overcome the attractive forces within the aggregates (Schomakers et al., 2015).

For a successful mechanical remediation, at the point of impact, the applied energy into the contaminant/solid interface must be greater than the potential energy that holds the contaminants on the solid surface. More hydrophobic contaminants are harder to be detached from the solid matter. Hydrocarbons with a lower relative molecular mass are easier to remove than heavier hydrocarbons (Bayley and Biggs. 2005a).

Particle size analysis indicated that the sediment samples in this study were formed mostly from colloid (51%), clay (31%) and silt particles (13%) and the rest from sand (0.2%). Abdel-Moghny et al. (2012) studied the effect of soil texture on the remediation of hydrocarbon-contaminated soils by washing. They reported that the highest oil removal efficiency was obtained for washing sand particles and the lowest for the clay loam. The attachment of oil contamination and fine

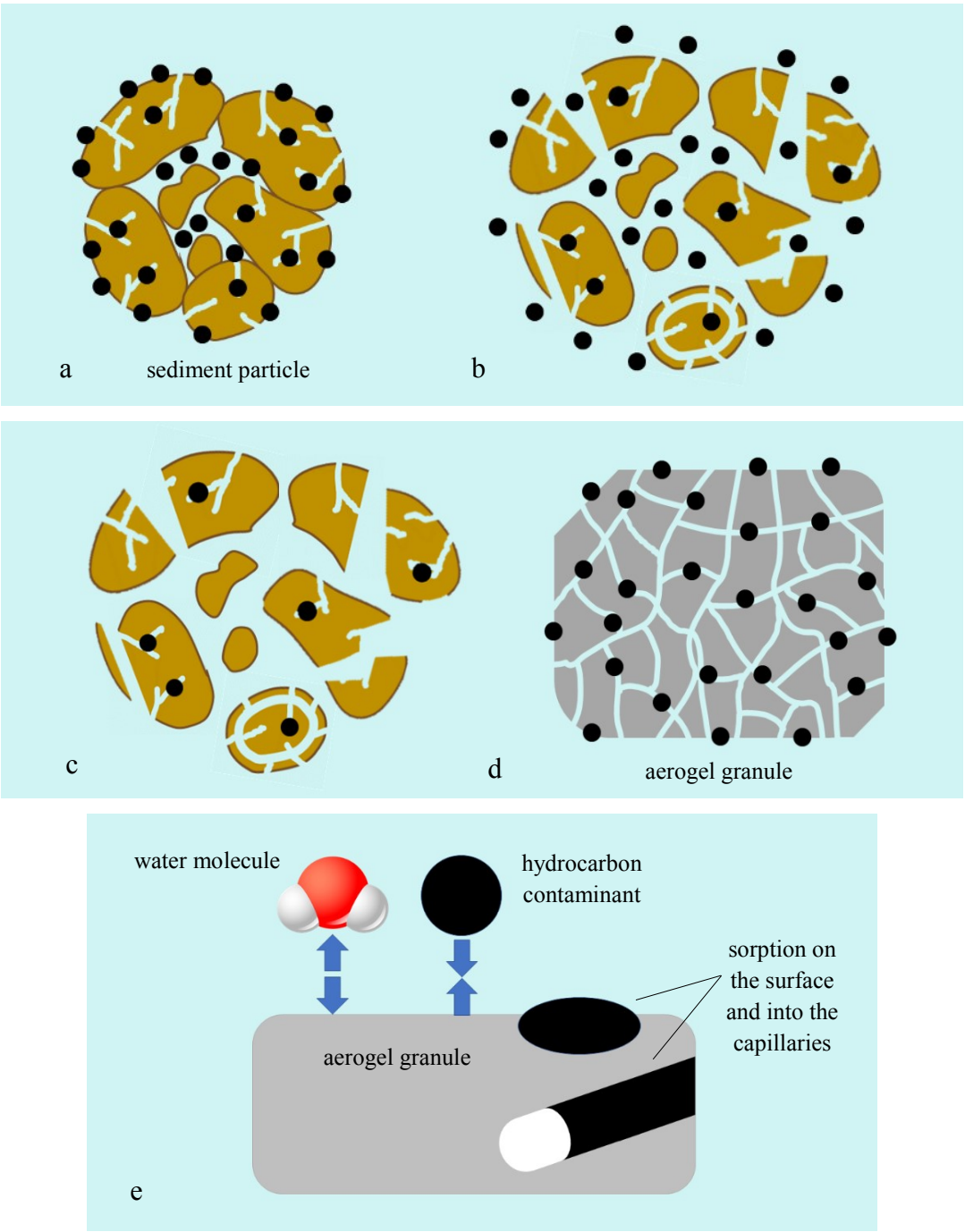


Figure 4.47. A simple schematic representation of desorption and sorption methodology: the hydrocarbon-contaminated sediment particles (a) shatter into smaller fragments due to breakage or attrition by vigorous agitation and the hydrocarbon contamination is released into the water (b). The remained sediment contains less concentration of contaminant (c); and the contamination is absorbed by aerogel (d) on the surface or inside the capillaries (e).

colloids forms very stable aggregates (Gong et al, 2014). Sun and Zheng (2009) reported that sediment particles with a diameter less than 5 μm are ready to form aggregates with spilled oil with stronger forces between oil and sediment, than the larger particles. Therefore, the removal of hydrocarbons for the sediment samples used in the current study can be considered a difficult sediment remediation process.

Sorption of contaminants by aerogel particles

The strong hydrophobic property of the modified aerogel surface was due to the existence of tri-methyl-silyl ($-Si(CH_3)_3$) groups on the surface of the aerogel network. These non-polar functional groups not only are not able to form hydrogen bonds with water but repel it (Soleimani & Abbasi, 2008). Hydrophobic silica aerogels have low energy surface, thus they are not wetted by water. But the organic liquids are less polarizable than the solid aerogel and can wet the surface and get absorbed by the aerogels (Venkateswara Rao et al., 2007). According to the GC peaks, the sediment samples in the present study were contaminated by an unresolved complex mixture (UCM) of hydrocarbons. UCM is a mixture of thousands of hydrocarbons with different molecular structures (Kondla et al., 2016; Monza et al., 2015). Water molecules may form only very weak non-polar inter-molecular forces with tri-methyl-silyl groups, but very strong ones with other water molecules. For this reason, water forms droplets on the surfaces of hydrophobic aerogels. Hydrophobic aerogels can float on water for months (Aegerter et al., 2011).

Sorption of TPH contaminants by hydrophobic silica aerogel was fitted with pseudo-second kinetics and the Freundlich adsorption model. Pseudo-second order model indicates the strong binding between the sorbate and sorbent similar the chemisorption, rather than the physisorption. The deeper investigation of sorption mechanism of chemisorption can be proved by estimation of the activation energies, from the kinetic experiments conducted at different temperatures, or by studying the dependence of the process rates on the sizes of sorbent particles. The Freundlich isotherm indicates a heterogeneous surface through a multilayer adsorption mechanism.

According to scanning electron microscopy (SEM) studies by Parale et al. (2011), the porosity of hydrophobic silica aerogel is about 90-95%. Hydrocarbons diffuse into this empty space by the effect of capillary forces. According to Hrubesh (2001), water-immiscible organic solvents wet the surface of the hydrophobic aerogels and are re-drawn into the porous by capillary forces. After

regeneration of aerogel molecules by organic solvents, the porous structure of the aerogel collapsed which dramatically reduced the adsorption capacity of aerogels (Figure 4.46 d and e).

4.7. Comparison with Conventional Adsorbents

Comparison of hydrophobic aerogels with other adsorbents used in previous studies leads to the improvement of the desorption-sorption process in the future research or in-field applications. Many conventional adsorbents, which are used for oil spill containment, sink after adsorption of oil (Fingas, 2011). The density of aerogels after adsorption of hydrocarbons in desorption-sorption process increased about 14% because of shrinkage of granules under the pressure of the slurry flow. This density was still much smaller than the density of water. Therefore, they could float on the surface of water and easily separated. The sorption capacity of aerogel granules used in the present study for light and heavy crude oil was 7.8 and 5.7 g/g, respectively that falls in the range of sorption capacities of suggested sorbents for the separation of oil from water in Table 2.3.

Due to the problem of fouling and sinking, adsorption pads cannot be used in sediment-in-water slurries. However, adsorption pads have a higher sorption capability and are cheaper. They could be easily recovered. Hydrophobic silica aerogels in the form of granules are very brittle and difficult to apply in-situ. They are not likely to be used in-situ unless they are produced in the form of pad and booms or be used in the packed columns.

4.8. Technology Roadmap

Many methods for remediation and management of contaminated sediments originate from soil remediation techniques (Mulligan, 2001a; Reible & Lanczos, 2006). Selection of the remediation technology is a complicated process and carried out based on many factors, particularly sediment type and contaminant type (Mulligan et al., 2009; Reible & Lanczos, 2006). Table 4.3 represents a list of selected conventional biological and physiochemical remediation methodologies for hydrocarbon-polluted soils and sediments.

Table 4.3. Selected list of conventional biological and physiochemical remediation methodologies for hydrocarbon-polluted soils and sediments (Fuentes et al., 2014; Mulligan et al., 2009)

Remediation method	**Treatment Site**	**Cost (US $/m^3)**
Biological		
Biostimulation	In-situ	30-100
Bioaugmentation	In-situ	30-100
Bioventing	In-situ	79-970
Biopiles	Ex-situ	130-260
Composting	Ex-situ	630-757
Landfarming	Ex-situ	30-70
Physiochemical		
Vapor extraction	In-situ	405-1,485
Stabilization – Solidification	In-situ	60-290
Thermal desorption	Ex-situ	44-252

Washing is one of the most common methods for decontamination of environmental solid media such as sediment, soil, coastal sands, mining and oil sands tailings, buried and subaqueous wastes, solid sludge and oil well drilling mud (oil sludge). The method has commercially been applied for remediation of a wide range of contaminants. Washing is a cost-effective method and does not require high technological know-how. At the same time, washing carries its drawbacks. Washing is not very efficient for cleaning fine particles of soil or sediment. Effluents contain residues of hazardous pollutants and need to be disposed of in a proper way. Washing with a solvent adds residues of chemicals to the soil and sediments. Sequential steps may be required for a desired contamination removal efficiency (Dermont et al., 2008; ICS-UNIDO, 2007; Mulligan et al., 2009).

Dredging as a very common technique possesses the adverse effect of destroying benthic habit. Dredging may remove contaminated sediments incompletely. Also, dredging can re-suspend contaminated fine particles into the water column. Furthermore, management and decontamination of the dredged sediments are very difficult (Reible & Lanczos, 2006). Amendment of sediments,

e.g. by conventional sorbents is a slow process and bears the risk of alteration of the alive species communities in the sediments (Ghosh et al., 2011; Qian et al., 2003).

Figure 4.47 represents the technology roadmap for the remediation of soils contaminated with poly-aromatic hydrocarbons (PAH) (Kuppusamy et al., 2017). Most soil remediation techniques are used for remediation of contaminated sediments, as well. The conventional methods may be replaced with advanced methodologies applying modified organisms and nanomaterials. In recent years, the application of organic and inorganic nanomaterials in environmental technology, particularly for removing petroleum hydrocarbons from water, has been the main focus of numerous research studies in environmental science and technology (Gautam, & Chattopadhyaya, 2016; Kharisov et al., 2014; Zhang et al, 2009). Maleki (2016) has reviewed the research on the application of different types of aerogels in sorption of pollutants from the environment (Table 2.5). The silica aerogel used in this study is manufactured by Cabot Inc. and its sorption capacity is similar to the first row of the table. The application of aerogels in research and industry will continue to grow in the coming years. According to a market research by IDTechEx (2017), the market value of aerogel production industry in the year 2017 was over $260 million and is anticipated to reach $910 million by 2027. Therefore, the current price of hydrophobic silica aerogel (15-25 USD/kg) will be decreased.

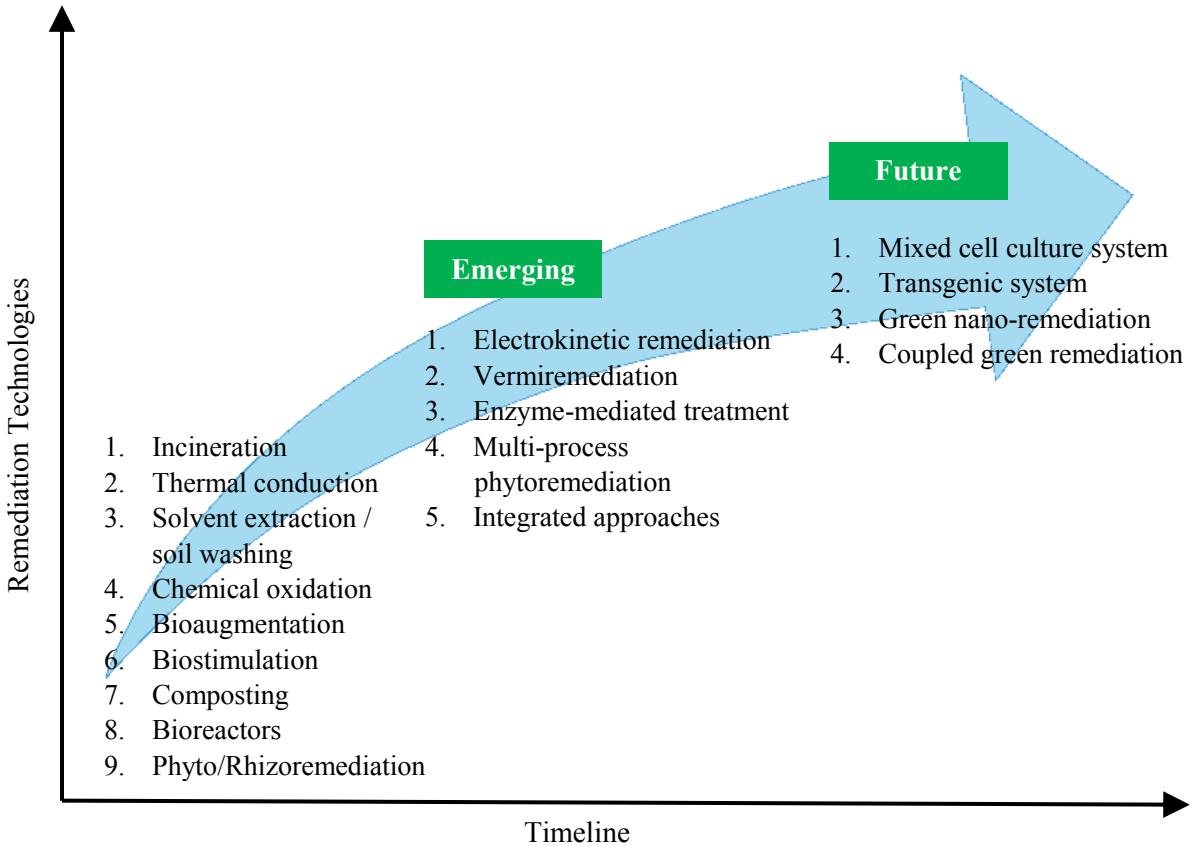


Figure 4.48. Remediation technology roadmap for PAH-contaminated soils (Kuppusamy et al., 2017)

4.9. Chapter Overview

The TPH contamination was in the form of Unresolved Complex Mixture (UCM) which indicated the aging of the contaminant over 5 decades of industrial activity. The results showed 29.5% TPH removal from sediment after 45 minutes of vigorous agitation in 15900 rpm. The leached TPH was adsorbed by the aerogel. The processed sediment and effluent water met Canadian governmental and provincial quality criteria for marine and fresh water. pH, solid load and retention time in the ranges that were applied in this study did not show a significant effect on the efficiency of the process. Higher agitation speed increased the leaching of hydrocarbons from sediments resulting in a higher exposed surface area to the slurry turbulence. Adsorption kinetics data suggested pseudo-second order kinetics. Adsorption data fitted with the Freundlich mechanism. The

sediment average particle size reduced after the desorption-sorption process, indicating the breakage and attrition of sediments. The surface of sediment and aerogel particles became coarser after the process. The sorption mechanism included the capillary diffusion of hydrocarbons into the porous structure of aerogels and affinity between the hydrophobic groups on the surface of modified aerogel and hydrocarbon contaminants (Figure 4.46)

The sediment quality including the content of heavy metals, nitrogen, and phosphorus did not change significantly. The concentration of heavy metals in the effluent water was lower the drinking and freshwater standards. Aerogels showed a low affinity towards the heavy metals. They decreased the concentration of total phosphorus and total Kjeldahl nitrogen in water. The attempt for regeneration of aerogels by organic solvents did not succeed. After 2 cycles of regeneration by heat, the adsorption capacity of aerogels decreased by 25% due to the decomposition of aerogel functional groups.

Chapter 5 – Conclusions & Recommendations

5.1. Conclusions

The desorption-sorption process can be considered as a fast method for remediation of petroleum hydrocarbons from sediments and compliant with sediment and water quality criteria. The method needs to be investigated in larger pilot setups and operating scale. Also, it needs to be approved by environmental regulatory bodies. pH, solid load and retention time in the ranges that were applied in this study did not show a significant effect on the efficiency of the process. Higher agitation speed increased the leaching of hydrocarbons from sediments. In higher temperatures, desorption from sediments increased but no significant effect was observed in aerogels sorption capacity. The cold environment was favored for sorption by aerogels and not favorable for desorption of hydrocarbons from sediments.

Adsorption kinetics data suggested a pseudo-second order kinetics. Adsorption isotherm data fitted with the Freundlich mechanism. The average particle size of sediments decreased after the desorption-sorption process. The surface of sediment and aerogel particles became coarser after the process.

The sediment quality including the content of heavy metals, nitrogen and phosphorous did not change significantly after the process. The concentration of heavy metals in the process water was significantly below the drinking and fresh water in Canadian and provincial standards. Hydrophobic aerogel granules showed a low affinity towards the heavy metals. They removed the very low concentrations of heavy metals from the solution to some extent. The final concentration of total phosphorus in desorption-sorption process water was less than when sediments were exposed to only agitation. Hydrophobic silica aerogels did not show any affinity toward inorganic

nitrogen, but they removed the small concentration of total Kjeldahl nitrogen from water. The attempt for regeneration of used aerogels by organic solvents failed because the porous network of aerogel granules collapsed after being exposed to the solvents. In the heat regeneration experiments, after 2 cycles of regeneration, the adsorption capacity of aerogels decreased significantly.

Currently, there are synthetic sorbents for cleaning up the oil products. These sorbents absorb water and oil and sink after a period of time. In a technology assessment view for sediment remediation, the most desirable option is avoiding dredging or minimizing the dredged quantity. The desorption-sorption methodology needs to be investigated at larger scales. If the agitation is generated more efficiently in a tank, it may be more economical to be used on-site or ex-situ. Still, the main advantage of not introducing a chemical substance into the natural environment remains.

5.2. Recommendations for Future Studies

In this study, the desorption-sorption process as a closed-loop remediation methodology was introduced for the first time. The TPH-contaminated sediments were selected as an environmental solid medium. As well, surface-modified hydrophobic silica aerogel was chosen as an adsorbent. The research in this area can continue by investigating different solid media, contaminants or sorbents. Also, the effect of various factors can be studied deeper. For example, the research may be pursued on:

- Application of various types of natural, mineral and synthetic sorbents in the desorption-sorption process
- Applying the desorption-sorption methodology on the other environmental solid media such as remediation of hydrocarbon-contaminated soils, coastal sands after oil spills, extraction of bitumen from oil sands tailings, separation of oil from solid sludge and oil-well drilling mud
- Application of the desorption-sorption process for the sorption of heavy metals, phosphorous and nitrogen from soils or sediments

- Investigation of the effect of type, the content, the aging and weathering of the contamination in solid media on the efficiency of the desorption-sorption.

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Appendix I

The map of Sector 103, Port of Montreal (Google Map, 2014)